THE

CHEMICAL NEWS

AND

JOURNAL OF PHYSICAL SCIENCE.

WITH WHICH IS INCORPORATED THE "CHEMICAL GAZETTE."

A Journal of Practical Chemistry

IN ALL ITS APPLICATIONS TO

PHARMACY, ARTS, AND MANUFACTURES.

EDITED BY

SIR WILLIAM CROOKES, O.M., D.Sc., F.R.S., &c.

VOLUME CVIII.—1913.

LONDON:

PUBLISHED AT THE OFFICE, 16, NEWCASTLE STREET, FARRINGDON ST.,

E.C.

AND SOLD BY ALL BOOKSELLERS.

MDCCCCXIII.

LONDON:
PRINTED BY EDWIN JOHN DAVEY,
16, NEWCASTLE STREET, FARRINGDON STREET,
E.C.

THE CHEMICAL NEWS.

VOLUME CVIII.

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No. 2797.—JULY 4, 1913.

THE RECENT DEVELOPMENT OF NEUTRAL SALT REACTIONS.

By M. FORT.

ALTHOUGH the law of mass action is now of fundamental importance in chemistry, it is frequently neglected or imperfectly appreciated in its bearing on technical and analytical problems, and perhaps is less rarely looked to for an explanation of such than the everyday "common-sense" chemical notions which by constant use, as in routine work, often acquire high false values. Thus one readily thinks of caustic soda expelling ammonia from a salt in solution, but to think of ammonia expelling sodium as sodium hydrate from a sodium salt in solution creates some degree of mental confusion, greater or less according to one's actual familiarity with the potency of mass law.

It became known among chemists (the writer is unaware of the original source) that sodium sulphate and acetic acid, under certain conditions, may react as though free sulphuric acid is actually present. The experiment may be shown with methyl orange as indicator and a hot dilute solution of acetic acid. On adding sodium sulphate a colour change, denoting an increase in acidity, takes place, ascribable to the liberation of a small amount of free sulphuric acid by the action of the weaker acetic acid competing for the base combined in the salt. This reaction was known as the "neutral salt reaction," and was little heard of until recent years. It is a direct outcome of mass law and demands expression by means of a reversible equation:—

$$Na_2SO_4+2CH_3 \cdot COOH \rightleftharpoons 2NaOOC \cdot CH_3+H_2SO_4.$$

The equilibrium is determined mainly thus $\leftarrow$, but it is never completed, hence the necessity for the presence of a small amount of free mineral acid, liberated by the weaker organic acid from the neutral salt in attaining equilibrium. As might be expected there is no need for the amount of free acetic to be large in order to get an appreciable amount of sulphuric acid formed, if the mass of sodium sulphate present be considerable. The reaction is favoured by rise in temperature, as this increases the extent of hydrolytic dissociation of the neutral salt, which dissociation is supposedly necessary before the neutral salt reaction can take place.

A further observation was made by L. L. Lloyd (*Journ. Soc. Chem. Indus.*, 1910, p. 1361), namely, that in a neutral salt reaction between formic acid and sodium sulphate, the presence of wool greatly increases the amount of sulphuric acid formed, in fact from a mere trace to a distinctly appreciable amount. Lloyd obtained some of the free acid from the wool by extraction with water. This is the first indication of the recognition of the important influence exerted by neutral salt reactions in technical chemistry.

Quite apart apparently from this work is an observation of Arndt's (*Zeit. Anorg. Chem.*, xxviii., 365), that by heating a strong solution of sodium sulphate with litmus an alkaline reaction is obtained. This was confirmed by Kraus (*Farb. Zeit.*, 1911, p. 333), and applied by him to explain certain phenomena connected with the dyeing of wool, *e.g.*, the deterioration of the wool fibre dyed in so-called neutral dye-baths with sodium sulphate as assistant. He could not, however, obtain similar alkalinity with sodium chloride, and Dreaper (*Journ. Soc. Dyers and Co.*, 1911, p. 293) suggested that the difference lay in the inability of sodium chloride to react in a similar way to the following:—

$$Na_2SO_4+H_2O \rightleftharpoons NaOH+NaHSO_4.$$

Later work has explained these observations in a more satisfactory way.

It appeared to the author that the known neutral salt reaction if correctly understood must have a counterpart in the reactions of weak bases with salts of stronger bases, and considerable evidence was acquired of such being the case (Fort, *Journ. Soc. Dyers*, 1912, p. 314). In the first place Arndt's observation was confirmed, using also alizarin as indicator, and a series of salts classified on the basis of alkalinity or the absence of an alkaline reaction at the boil. Later it was shown by the author, after extending his knowledge of neutral salt reactions, that the supposed alkalinity of sodium sulphate at the boil is not due to special conditions of ionisation determined by rise in temperature, as was tentatively suggested by Procter (*Journ. Soc. Dyers*, 1913, p. 40), but is part of a neutral salt reaction with the acidic indicator, *e.g.*, in the case of alizarin a small quantity of coloured sodium alizarate is formed, and a similar explanation covers the reaction with litmus. On cooling the colour disappears, due to a reversal of the reaction. Since sodium chloride is the salt of a stronger acid than sodium sulphate it is not so readily hydrolysed and decomposed by alizarin, and hence shows no colour reaction at the boil. However, by using a more strongly acid indicator, for example di-nitro-anthrachrysone-di-sulphonic acid, a distinct alkaline colour reaction was obtained with sodium chloride at the boil. Further, it was shown that by using as indicator a drop or two of a dilute solution of rosaniline base carefully decolorised with very dilute caustic soda, on heating with a solution of sodium chloride or sulphate a pronounced magenta colour appeared, *i.e.*, an acid reaction was given. In fact there is no evidence of the supposed alkalinity of sodium sulphate solution at the boil, apart from a neutral salt re-

action with the indicator used, which agrees with the apparently surprising fact that the same sample of sodium sulphate may be made to show either an acid or an alkaline colour reaction in hot solution according to whether the indicator be respectively basic or acid in character. In this type of reaction the presence of water is regarded as essential to give hydrolytic dissociation of the salt which is increased greatly as temperature rises, with the result that the free weak acid or base can compete for base or acid respectively as the case may be, formed from the salt by hydrolysis, thereby causing the formation of more or less of the free strong acid or base from the salt. The former phase of the reaction is seen in the colour indications obtained from sodium sulphate as described above.

The latter phase of the neutral salt reaction, *i.e.*, the liberation of varying small quantities of strong acids or bases by the interaction of solutions of their salts with weaker acids or bases, is of great technical interest.

A new neutral salt reaction was described by the author (1912, *loc. cit.*), who found that on adding sodium sulphate or chloride to a boiling aqueous solution of aniline in a platinum dish, containing alizarin as indicator, an alkaline colour reaction was obtained at once. This is assumed to be due to two reactions :—

$$\text{(i.) } NaCl + H_2O \rightleftarrows NaOH + HCl.$$

$$\text{(ii.) } C_6H_5{\cdot}NH_2 + HCl \rightleftarrows C_6H_5{\cdot}NH_2{\cdot}HCl.$$

Similar reactions were obtained with a variety of organic bases, and also one found it possible to show even the ability of ammonia to release caustic soda in a solution of a neutral sodium salt. Phenolphthalein was used as indicator, and as is well known it reacts feebly and incompletely with ammonia in dilute solution; in fact the pink colour obtained in the cold fades on warming, due presumably to increased hydrolysis of the rather unstable coloured compound as temperature rises. The same influence, however, promotes the neutral salt reaction, as was explained previously. If, then, a dilute solution of ammonia be taken of such a strength as to give a faint pink colour with phenolphthalein at the boil, on adding sodium sulphate or sodium chloride to the hot solution a much deeper pink is at once shown. The experiment may be varied by starting with two portions of cold dilute ammonia just strong enough to give a colour with phenolphthalein, to one portion sodium chloride being added before gently heating. The portion containing the neutral salt may be shown to remain pink up to the boil, while the other fades on warming through a few degrees. On cooling a similar shade is regained in each case.

The author has been led to believe also in another type of reaction, *i.e.*, the double neutral salt reaction which must take place in solution, between any two neutral salts obtained from different acids and bases, resulting in the establishment of an equilibrium in which all four possible salts of these acids and bases are concerned. For example, it is found that neither calcium sulphate nor sodium chloride give a colour reaction when a solution is boiled with alizarin as indicator, the contrary being the case with sodium sulphate, as was mentioned. However, by adding sodium chloride to a boiling solution of calcium sulphate in a platinum dish, the crimson alkaline reaction with alizarin is obtained. This is explained as due to an equilibrium involving the formation of appreciable quantities of calcium chloride and sodium sulphate, sufficient to give the above colour reaction.

Technical and other Applications.

There has been rapid application of the knowledge of these reactions to industrial problems. Procter has applied it to the pickling of hides (*Collegium*, 1912, No. 512, p. 687), and has shown that N/10 formic acid along with common salt can fix in gelatin an amount of hydrochloric acid equal to that taken up from N/10 hydrochloric acid itself. L. L. Lloyd has also adequately explained the formation and avoidance of salt stains on hides by means of neutral salt reactions (*Collegium*, 1913, No. 517, p. 188), and also the occurrence of tendered cotton threads in half wool unions after dyeing in a bath containing as assistants formic acid and Glauber's salt. This latter instance may be used to show how the knowledge recently acquired may solve very troublesome technical difficulties. It was well established and accepted that formic acid does not tender cotton, and it found favour with dyers largely on account of this great advantage which it possesses over sulphuric acid. It is a matter of equal faith that sodium sulphate alone causes no deterioration of the cotton fibre, and apparently no one saw any reason why danger should be apprehended when these assistants were used together; indeed, although occasional tendering of batches of goods occurred where it was most difficult to avoid the correct or something approaching the right conclusion, the "common-sense" view of the impossibility of a weak acid like formic setting free sulphuric acid, seems to have prevented its being reached. Lloyd showed that not only is sulphuric acid produced, but being absorbed by the wool present the reaction is much more considerable, and free sulphuric acid can be extracted from the fabric with water in appreciable amount. By a thorough rinsing after dyeing, troubles from this cause may be largely obviated.

The author has shown that wool itself can to some extent decompose even such stable salts as sodium sulphate in boiling baths, both the strongly basic and apparently weaker acid properties of the amphoteric fibre-substance being involved (*Journ. Soc. Dyers*, 1913, p. 80). The basic properties of wool are no doubt mainly responsible by causing the transference of sulphuric acid to the fibre, while the prevailing acidity of a portion of the wool or its hydrolysis products causes a part of the fibre to be dissolved away by the alkali constituent of the salt. This is the reason for the injury done to the lustre of wool when dyed in hot neutral baths containing Glauber's salt, which may be largely avoided by addition of glue to the dye bath. As may be well understood from what has been said, common salt is injurious to a less degree and is often preferred, *e.g.*, by garment dyers, on that account. Further, it was shown that a certain degree of tendering of cotton in a half-wool union fabric may be caused by a hot bath of sodium sulphate in the following way:—The wool combines with sulphuric acid obtained from the salt, as already explained, and retains a portion firmly in spite of washing with water, which on drying and storing is partly set free, in which state it tenders the cotton fibres present (*Journ. Soc. Dyers*, 1913, p. 120).

Very recently Lloyd has explained to the Society of Dyers and Colourists (London Section) the causes of certain defects in silk fabrics. Silk is found to decompose to some extent mineral halides in solution, forming halogen compounds with the silk fibre, from which later the free halogen may be liberated and give rise to oxidation and deterioration of the fibre on keeping.

The recent legislation against filthy flock for upholstery purposes has set up a minimum chlorine content as a standard of purity, which, however, it is found may be approached by fresh clean wool (*Journ. Soc. Chem. Ind.*, 1913, p. 402), a discovery which, in the light of what has been said, may be accounted for by conditions on the live sheep, *i.e.*, the presence of organic acids and mineral chlorides from perspiration. The ordinary perspiration test applied to dyed fabrics is a treatment with weak acetic acid, and has proved to be quite inadequate for practical conclusions to be drawn. The author has for some time replaced this test in his own laboratory by a test employing common salt in conjunction with acetic acid, and may now recommend it for use where the ideal one of actual wear is inapplicable. A similar modification for the purposes of an alkaline perspiration test might be arranged, *e.g.*, for horse cloths.

The physiological interest attached to the neutral salt reactions is necessarily great, but at the present one may

not dogmatise much. However, it is clear *à priori*, for example, that organic acids of the stomach or fruit acids in presence of common salt or mineral chlorides taken with food, will set up an equilibrium in which free hydrochloric acid will play a part, and in which albuminoids also present can favour the production of this mineral acid (compare the effect of hide, wool, and silk substance in this connection), which being required for digestion of these same albuminoids, will be produced as required in complete accordance with beneficent natural law. In regard to the known secretion of hydrochloric acid from special glands, as distinct from its formation by reactions among the contents of the stomach, the amount of sodium chloride in the blood forming a permanent reserve may be looked to as the starting material, and a neutral salt reaction as the most likely chemical means to be employed. The author has not been afforded opportunity of an experimental justification of this view, as was originally intended, owing to a greater personal interest in the rapidly developing textile applications of the knowledge of neutral salt reactions. This knowledge has suggested an explanation of a root difficulty in the acceptance of the chemical theory of dyeing, namely, as to how a free colour acid, the dyeing of which on wool is greatly promoted by a previous treatment of the fibre with sulphuric acid, can effect combination with wool already combined with a strong acid. In the author's opinion the first part of the answer to this is that the partial hydrolysis of the wool by the acid causes a great increase in the available basic parts of wool, and secondly, that local conditions in or on the fibre favour a reaction offering great analogy with neutral salt reactions, for it is found that wool, after treatment with sulphuric acid and then with water till no more acid is removed by extraction, will readily absorb free colour acids, *e.g.*, picric acid and certain azo-sulphonic acids, at the same time liberating an appreciable amount of free sulphuric acid, not necessarily equivalent in amount but at any rate somewhat similar. Fuller evidence acquired in this matter will be published at an early date.

These are the main features of the development of the knowledge of neutral salt reactions, and of its ready application to a diversity of subjects, and in the latter connection considerable progress may still be looked for.

Technical College, Bradford.

REFORM OF CHEMICAL CALCULATIONS.

By C. J. T. HANSSEN.

IN CHEMICAL NEWS, November 1, 1912 (vol. cvi, p. 215) are collected from the last fifteen years atomic weights given in plain figures, and there arranged into a kind of atomic weight table; the author has now extended this list to 76 elements, and respectfully invites chemists to investigate this table, which, if proved and accepted, would very much simplify chemical calculations and operations.

International Atomic Weights, 1913.

1. Hydrogen	H	1
2. Helium	He	4
3. Lithium	Li	7
4. Glucinium	Gl	9
5. Boron	B	11
6. Carbon	C	12
7. Nitrogen	N	14
8. Oxygen	O	16
9. Fluorine	F	19
10. Neon	Ne	20
11. Sodium	Na	23
12. Magnesium	Mg	24
13. Aluminium	Al	27
14. Phosphorus	P	31
15. Sulphur	S	32
16. Chlorine (35·46)	Cl	?
17. Potassium (39·10)	K	?
18. Calcium	Ca	40
19. Scandium	Sc	44
20. Titanium (48·1)	Ti	?
21. Vanadium	V	51
22. Chromium	Cr	53
23. Manganese	Mn	55
24. Iron	Fe	56
25. Nickel (58·68)	Ni	?
26. Cobalt	Co	59
27. Copper (61·57)	C	?
28. Zinc (65·37)	Zn	?
29. Gallium	Ga	70
30. Germanium (72·5)	Ge	?
31. Arsenic	As	75
32. Selenium	Se	79
33. Bromine	Br	80
34. Krypton (82·9)	Kr	?
35. Rubidium (85·7)	Rb	?
36. Strontium (87·6)	Sr	?
37. Yttrium	Yt	89
38. Zirconium (90·6)	Zr	?
39. Columbium	Cb	94
40. Molybdenum	Mo	96
41. Ruthenium	Ru	102
42. Rhodium	Rh	103
43. Palladium	Pd	107
44. Silver	Ag	108
45. Cadmium	Cd	112
46. Tin	Sn	119
47. Antimony	Sb	120
48. Iodine	Io	127
49. Xenon	Xe	128
50. Cæsium	Cs	133
51. Barium (137·7)	Ba	?
52. Lanthanum	La	139
53. Cerium	Ce	140
54. Neodymium (144·6)	Nd	?
55. Samarium	Sa	150
56. Europium	Eu	152
57. Gadolinium	Gd	156
58. Terbium	Tb	160
59. Dysprosium (162·5)	Dy	?
60. Erbium	Er	166
61. Thulium	Tm	171
62. Ytterbium	Yb	173
63. Lutecium	Lu	174
64. Tantalum	Ta	181
65. Tungsten	Wo	184
66. Osmium	Os	191
67. Iridium	Ir	193
68. Platinium	Pt	195
69. Gold	Au	197
70. Mercury	Hg	200
71. Thallium	Tl	204
72. Lead	Pb	207
73. Bismuth	Bi	208
74. Radium	Ra	225
75. Thorium	Th	233
76. Uranium	U	240

Copenhagen, Valdemarsgade 3.
June 23, 1913.

Synthesis of Borides in Vacuum Furnace.—E. Wedekind.—The electric vacuum furnace can be used to effect syntheses of simple compounds of metals of high melting-point provided that the mixture is pressed into rods and these conduct the current sufficiently. This condition is fulfilled with mixtures of many metals with boron and the following borides have been prepared thus:—Zirconium boride, Zr_3B_4; vanadium boride, VB; uranium boride, UB_2. Experiments with molybdenum and titanium were failures.—*Berichte*, xlvi., No. 5.

THE SCIENTIFIC WEEK.

(*From Our Paris Correspondent*).

New Method to Foretell the Weather: The Guilbert Method (Hitherto Unpublished).

For the last few years a new method for forecasting the weather, the Guilbert method, has daily been enregistering new successes. Scientific men, such as Prof. Bernard Brunher, formerly Director of the Puy-de-Dôme Observatory, M. Violle, the learned physician, member of the French Institute, and the late Tersserenc de Bort, already very justly appreciated the meteorologist Gabriel Guilbert.

Violently controverted by the Control Meteorological Bureau of France, M. Guilbert has, however, received numerous encouragements from abroad. At Hamburg, at Valencia in Spain, at Belt in Holland, and also in Portugal, the meteorological observatories use his method of foretelling the weather.

In what does this method consist? M. Guilbert himself thus explains it to us:—The method of foretelling the weather at short spaces of time, known under the name of the Guilbert weather, is simply based on observation. M. Guilbert believes that the wind on the surface of the globe is the *cause*, at least apparent, of barometrical variations at twenty-four hours distance. So then, according to him, there is a relation of cause and effect between the speed and the direction of *superficial* winds and the consecutive variation of the pressure. Hence it is easy to conceive all the importance of this relation, if we consider that weather, in the widest sense of the word, depends, theoretically, on barometric pressure, and especially on the respective disposition of the centres of high and low pressure.

The essential aim of the method is precisely the prevision of forecast of these oscillations of pressure, to arrive at which it employs a certain number of rules. The method is, however, extremely simple, in this sense, that it requires only one single observation, that of the wind, the easiest of all, but over vast extents as over a large part of Europe for example. This method eliminates all other indications; it does not take into consideration the thermometrical or hygrometrical variations, the zones of rain or of fine weather; it leaves aside the winds of mountains and high regions as well as the atmospherical calorific or magnetic observations. Of all the elements generally considered in daily forecasts of the weather this method utilises only the *wind* and the variation of pressure.

But if the fundamental basis of the method is thus very simple, the application of the rules is more complicated and requires a veritable study. At the outset it is necessary to discern the different relative or absolute speeds of the surface winds, so as to discover the winds that the method designates as normal and abnormal, as convergent and divergent.

According to classical teaching, the wind is proportional to the gradient, that is to say, to the atmospherical slope, to the declivity of the air, so to say, compared with the declivity of the ground. The greater the importance of the slope, that is to say of the gradient, so much the more does the wind acquire speed. Now, M. Guilbert has remarked that on many days this notion was inexact. With a steep gradient, the wind remained weak, and inversely blew with force when the gradient was but weak.

It is from this observation M. Guilbert has deduced the fundamental principle of his method: the principle of *normal wind*. Normal wind is merely wind proportional to the gradient; abnormal wind will be so *by excess* if the wind is stronger than the gradient allows for theoretically, they will be abnormal by default if they are too weak. Now, winds abnormal *by excess* determine a barometrical rise, generally proportional to the abnormality observed in the twenty-four hours. Inversely the winds abnormal *by default* determine a fall of the barometer. Now a determining of these mere movements of barometric pressure allows the forecast of the future of squalls, and also makes it possible to know if such or such depression will be filled up or hollowed out, and if consequently the wind is going to increase or decrease. In certain circumstances, when the abnormal winds *by excess* surround a centre of depression, this centre is completely destroyed: tempestuous winds sometimes—and thus the method foretells—are followed by a perfect calm in a delay of twenty-four hours, sometimes even in twelve hours. It is the phenomenon called in the Guilbert method by the name of "Compression of the Cyclone."

The distinction of the winds designated as convergent and divergent is not less important. The former have a tendency to contract the depression, to push it back, they constitute a resistance of the invading march of the cyclone or tend to destroy it; the latter, on the contrary, are attractive winds; they constitute centres of attraction of less resistance: they determine the fall of the barometer and sometimes even create a hurricane.

Wind, both generator of tempests and calms; wind considered as the only regulator of atmospheric pressure tending ceaselessly to level if it is possible to thus express the idea—the aerial layers, such is the directing hypothesis of the Guilbert method.

The large proportion of successes obtained in the forecasts of the weather according to the above related principles shows incontestably that this point is the result of mechanical effects due to the mere action of the surface winds.

A Disease of Metals.

The first contagious disease of metals was discovered several years ago, by some chemists, on tin. The disease of tin is now well known. Prof. Hanriot, Director of the Metal Tests at the French Mint, has just recently discovered a new disease with which alloys may be afflicted. The alloy (copper-aluminium), containing 97 per cent of aluminium and 3 per cent of copper, which hardens the former of the two metals, is employed especially in the manufacture of helmets and other military objects and utensils. Now, in the Government stores and depôts, especially at Orleans, it has just lately been observed that thousands of copper-aluminium utensils are affected with this epidemic disease, which spreads from one object to another, corroding the metal and making holes in it. As the French War Department possesses about 25 to 30 millions worth of francs of objects manufactured with this alloy, measures have been taken to discover the origin of the evil. MM. Hanriot and Le Chatelier, the learned chemist of the Academy of Sciences, have been asked to elucidate the problem.

According to M. Chatelier the origin of the disease is due to a defect in the cold-hammering, but this opinion did not resist the experiments of M. Hanriot, who noticed that the copper-aluminium alloy was not stable. In certain conditions a veritable *migration of the copper* takes place. The copper emigrates to form, with the aluminium, a bronze of aluminium (50 per cent of aluminium and 50 per cent of copper), which is a stable alloy. But by this emigration there are formed on the surface of the metal holes with sides sometimes as long as 2 centimetres.

This disease spreads by contact, and the metal suffering from it looks as if it were attacked by eczema. A light grey spot appears at irregular intervals. The object may then be considered as lost and done for, as up till the present time no remedy is known for this singular affection.

A New Stereoscope.

When you look into an ordinary stereoscope there is a dissociation between the convergence which is preserved and the accommodation which is suppressed, by reason of the presence of the eye-glasses. Moreover, these latter and their mountings are a little joined to the effect produced, and the eyes cannot manage to get entirely free from them. Then, again, stereoscopic images are always small, and it is only, thanks to the enlargement by the

lenses of the eye-glasses, that the objects are seen at their real angle, so that the vision through a stereoscope is, as it were, a vision seen through a magnifying glass. For all these reasons the vision through a stereoscope differs sensibly from the normal vision. M. André Cheron, in a notice sent to the Academy of Sciences by Prof. Lipmann, shows that he has managed to construct a stereoscope whose aim is in a certain measure, as far as possible, to correct these inconveniences. The two pictures are projected on to one plane by two objectives of the same focus. Moreover, the two images are concentred and superposed on their plane of projection, thanks to the presence of an achromatic lens covering the two objectives projecting the images. On the plane of the formation of the images is a condensor, which makes the rays coming from the right picture converge towards the right eye, and those proceeding from the left picture towards the left eye. In this way the spectroscopic relief is integrally preserved and the eyes converge and accommodate themselves as if they were looking at objects really situated in space. The pictures are enlarged and looked at at the distance of distinct vision, without anything being interposed between them and the eyes of the observer.

The Contamination of Milk.

We all know how easily milk is contaminated. MM. Trillat and Fouassier, of the Paris Pasteur Institute, in a work on the frequency of the contamination of fresh milk by water containing infinitesimal quantities of typhoid bacilli, have recognised that the contamination might also take place even with water which from a bacteriological analysis might be declared healthy and sound. The typhoid bacillus is unperceived during the first hours of contamination. The development of the culture then takes place quickly, as it were, like an explosion.

MM. Trillat and Fouassier establish the fact that in its turn milk may become a frequent cause of the contamination of water in many circumstances, and this observation brings out clearly the reciprocal influence of water and of milk for their mutual typhoid fertilisation.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, June 19th, 1913.

Sir Archibald Geikie, K.C.B., President, in the Chair.

Papers were read as follows:—

"*Atomic Specific Heats between the Boiling-points of Liquid Nitrogen and Hydrogen. I. The Mean Atomic Specific Heats at 50° Absolute of the Elements a Periodic Function of the Atomic Weights.*" By Prof. Sir James Dewar, F.R.S.

"*Active Modification of Nitrogen Produced by the Electric Discharge.*" (V.). By Hon. R. J. Strutt, F.R.S.

1. An improved practical method of preparing and storing nitrogen for the experiments is described.

2. It is shown, notwithstanding criticisms of certain other experimenters, that the presence of traces of oxygen in the nitrogen used is not essential, or even favourable, to the phenomena. The nitrogen used, purified by cold phosphorus, does not contain oxygen to the extent of 1 part in 100,000. Passing it over red-hot copper in addition makes no difference. The intentional addition of oxygen does harm; 2 per cent obliterates the effects altogether. Hydrogen and carbon dioxide as impurities are much less harmful, but traces even of water vapour have a very bad effect.

3. Nitrides are formed by the admixture of active nitrogen with vapour of mercury, cadmium, zinc, arsenic, sodium, and sulphur. These are decomposable by water or potash solution, yielding ammonia.

4. Carbon disulphide yields a blue polymeric nitrogen sulphide, and polymeric carbon monosulphide. Chloride of sulphur gives ordinary yellow nitrogen sulphide. Stannic chloride and titanium tetrachloride also yield solid products. In the latter case nitrogen was proved to be present.

5. All organic compounds tried, except carbon tetrachloride, yield hydrocyanic acid freely, but not cyanogen, as was proved by chemical tests. When chlorine is present, cyanogen chloride is formed. Benzene yields (almost certainly) cyanobenzene.

6. The intensity of the cyanogen spectrum with organic compounds is no index of the quantity of hydrocyanic acid being formed. Preponderance of the red cyanogen bands is associated with cyanogen chloride or bromide.

On a general view of the evidence, there does not appear to be any definite connection between the development of spectra by active nitrogen and the chemical actions in progress.

"*Electrical Emissivity and Disintegration of Hot Metals.*" By Dr. J. A. Harker, F.R.S., and Dr. G. W. C. Kaye.

Preliminary experiments have been carried out on the volatilisation and electrical emissivity of a number of metals, mostly in nitrogen at reduced pressures. The metals were heated by alternating current and no applied potential was employed.

1. The emission of positive electricity occurs at temperatures from about 1000° to 1400° C. For metals which melt within this range, a sudden and marked increase in the positive current often occurred at the liquefying point —due, probably, to the sudden release of occluded gas.

2. Oxygen appears to augment the positive current.

3. At higher temperatures, negative electricity predominates and increases rapidly with the temperature. The negative current attained with iridium at the melting-point was 80 milliampères, with tantalum at 1670° C. 220 microampères, with iron at the melting-point 90 microampères. In the case of carbon in air at atmospheric pressure, an ionisation current of 3½ ampères was obtained.

4. The negative current at moderate pressures appears to be largely increased if the conditions are such that considerable sputtering of the metal occurs.

5. The negative currents are probably a consequence of chemical reaction between the metal and the surrounding gas.

6. Carbon becomes plastic in the neighbourhood of 2500° C. At such temperatures it also readily sublimes.

"*Method of Measuring the Viscosity of the Vapours of Volatile Liquids, with an Application to Bromine.*" By A. O. Rankine, D.Sc.

In this method of determining viscosities the rate of transpiration of the vapour through a capillary tube is controlled by the vapour pressures of the liquid itself, a difference of pressure being established in the process of virtually distilling the liquid through the capillary.

The pressures can be estimated without the use of mercury gauges—a state of affairs especially desirable in the case of the halogens.

The viscosities of unsaturated bromine vapour over the approximate range 10° C. to 250° C. have been measured, and, except at the lowest temperatures, are found to agree well with Sutherland's formula, notwithstanding the fact that all the temperatures are below the critical.

The constancy of the proportion $\eta_c{}^2/A$ (η_c = viscosity at critical temperature; A = atomic weight), as compared with chlorine, has been tested, and the agreement is good.

"*Efficiency of Selenium as a Detector of Light.*" By E. E. Fournier d'Albe.

The efficiency of a selenium preparation used as a detector of light is defined as the amount of additional conductivity imparted to it by the unit of incident light. It is best stated in "micro-ohms" per lumen. Since many factors affect the efficiency of a given selenium bridge, standard conditions are chosen, chief among them being an illumination of one lux. The law of light action is

studied, and the total effect is shown to be proportional to the square root of the incident energy, while the instantaneous effect is proportional to the energy. This is verified down to an illumination of 0·00001 metre-candle. It is shown that selenium is the most efficient light detector known, that it is capable of discriminating minute differences of luminous intensity far beyond the capacity of the eye, and that, with suitable means of detecting minute currents, it should offer a means of testing the quanta theory of light by direct experiment.

"*The Hall Effect in Liquid Electrolytes.*" By A. E. Oxley.

Experiments have been made on aqueous solutions of copper sulphate, silver nitrate, cadmium sulphate, and on copper sulphate gel. Each substance was placed in a small cell of glass or mica, and was subjected to a uniform magnetic field. A Paschen galvanometer was used to measure the transverse potential difference. In a uniform magnetic field this transverse potential difference is due partly to a true Hall effect (depending on the difference of the ionic mobilities) and partly to a concentration Hall effect (depending on the sum of the ionic mobilities). The latter effect is primarily the one which has been measured in this research, and the former, which is smaller, is included. Eight experiments have been made, and the transverse potential differences, which changed sign on reversal of the magnetic field, have been found to agree with the calculated values. The relation between the transverse potential difference and the intensity of the magnetic field, for an aqueous solution of copper sulphate, is linear.

"*Displacements of the Particles and their Paths in some Cases of Two-dimensional Motion of a Frictionless Liquid.*" By Prof. W. B. Morton.

"*Diurnal Variations of the Earth's Magnetism produced by the Moon and Sun.*" By S. Chapman.

"*Electric Effect of Rotating a Magnetic Insulator in a Magnetic Field.*" By Prof. H. A. Wilson, F.R.S., and Marjorie Wilson.

"*Magnetic Materials in Claywares.*" By Arthur Hopwood.

The author has found that white, cream, grey, yellow, buff, red, or brown claywares are feebly or moderately magnetic owing to the presence of unfused grains of unchanged ferruginous minerals and fused globules of complex ferruginous silicates; while flashed, brindled, or blue claywares are always strongly magnetic owing to the presence of complex ferruginous silicate and finely disseminated magnetic oxide of iron.

The origin of the complex ferruginous silicates in claywares is quite different from that of the magnetic oxide of iron. While the latter is produced either by the orientation of the magnetite, originally present in the clays, or by the reducing action of the kiln gases on the precipitated or colloid oxides, hydroxides, or carbonates of iron disseminated throughout the clays, the former are produced by the fusion of the granular or concretionary ferruginous minerals, *i.e.*, iron pyrites, siderite, hæmatite, magnetite, biotite, &c., occurring in the clays with the surrounding matrix. When clays are heated in strongly oxidising kilns ranging in temperature from 600° to 1000° C. they become magnetic owing to the orientation of unchanged magnetic minerals, and when heated in strongly oxidising kilns ranging in temperature from 1000° to 1350° C. they become magnetic, partly owing to the orientation of unchanged magnetic minerals and partly to the conversion of granular or ferruginous minerals to complex ferruginous silicates; but when clays are heated in reducing kilns ranging in temperature from 600° to 1350° C. they become magnetic owing to the formation of complex ferruginous silicates and magnetic oxide of iron.

The amounts of the magnetic materials present in the different sorts of claywares made in various parts of the country show that great care must be exercised in the selection of the materials for the construction of physical laboratories and magnetic observatories, or serious disturbances may take place during observations with delicate magnetic instruments.

"*Synthesis of the Anhydrides of α-Aminoacyl Glucosamines.*" By Arthur Hopwood and Charles Weizmann.

"*Flexure of Telescope Mirror Discs arising from their Weight, and its Influence upon Resolving Power.*" By H. S. Jones.

"*On Fourier Series and Functions of Bounded Variation.*" By Prof. W. H. Young, F.R.S

"*Condition that a Trigonometrical Series should have a certain Form.*" By Prof. W. H. Young, F.R.S.

"*Trigonometrical Series whose Cesaro Partial Summations Oscillate Finitely.*" By Prof. W. H. Young, F.R.S.

CHEMICAL SOCIETY.

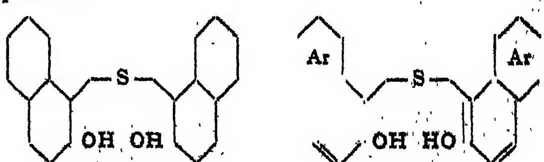
Ordinary Meeting, June 5th, 1913.

Prof. W. H. Perkin, LL.D., F.R.S., President, in the Chair.

(Concluded from vol. cvii., p. 311).

184. "*β-Naphthol Sulphide and iso-β-Naphthol Sulphide; and the Constitution of β-Naphthol.*" By Thomas Joseph Nolan and Samuel Smiles.

The results of previous experiments were used in discussing the constitution of the two sulphides. It was concluded that the normal sulphide is the true α-sulphide of β-naphthol (I.), whilst the *iso*sulphide, which is formed by reducing naphthasulphonium-quinone, is represented as in II., and may be regarded as the hydrosulphonium-quinone:—



I. II.

The constitution of β-naphthol was also discussed, and it was concluded that in this substance, and probably also in naphthalene, the hydrocarbon nucleus exists in a symmetrical condition.

185. "*Nitrites of Thallium, Lithium, Cæsium, and Rubidium.*" By Walter Craven Ball and Harold Helling Abram.

Thallous nitrite, $TlNO_2$, is a bright orange-red soluble crystalline salt.

Hydrated lithium nitrite crystallises with 1 molecule of water, as stated by Rây (*Proc.*, 1908, xxiv., 75).

Cæsium nitrite, previously examined by Jamieson (*Am. Chem. Journ.*, 1907, xxxviii., 616) closely resembles the potassium salt, as also does rubidium nitrite.

186. "*Note on the Fat of the Seeds of* Oncoba echinata; *Occurrence of Chaulmoogric Acid.* By Ernest Goulding and Noel Charles Akers.

Samples of the seeds of the "Gorli" plant (*Oncoba echinata*, Oliver) have been received at the Imperial Institute from Sierra Leone, and have been examined with the following results.

The seeds contained 5·8 per cent of moisture, and, on extraction with light petroleum, yielded about 47 per cent of a hard opaque white fat of a crystalline appearance and possessing a peculiar characteristic odour. The fat furnished the following constants: D100°/15·5° 0·898, $[\alpha]_D$ /17 +48·8°; acid value, 4·5; saponification value, 192·4; iodine value, 99·7; Hehner value, 96·5; Reichert-Meissl value, nil; unsaponifiable matter, 1·5 per cent. It

had no definite melting-point, but gradually liquefied above 35°, and was completely melted at 45°.

The fatty acids obtained by hydrolysing the fat had an iodine value of 105·1, $[\alpha]_D$ /18 +52·5°, and consisted of a mixture of a crystalline solid and a liquid. By pressing the mixture between folds of filter-paper, a large proportion of the solid substance could be separated, and on re-crystallisation from warm alcohol it was obtained in thin lustrous plates, melting at 69°. This acid gave an iodine value of 90·5, and $[\alpha]_D$ /17 +60·0°; it was identified as chaulmoogric acid, $C_{17}H_{31}{\cdot}CO_2H$ (Power and Gornall, *Trans.*, 1904, lxxxv., 846), by the analysis of the silver salt and the preparation of the methyl ester, which melted at 22°, and had $[\alpha]_D$ /21 +55·8°.

The liquid portion of the fatty acids, although saturated with chaulmoogric acid, gave an iodine value of 122, showing that the liquid acids are highly unsaturated; it darkened rapidly on exposure to the air.

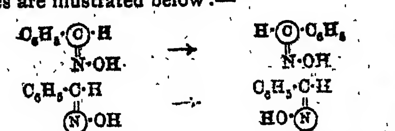
The investigation showed that the fatty acids consisted approximately of chaulmoogric acid, 87·5 per cent, and liquid acids, 12·5 per cent.

187. "*A New Model to Illustrate the Walden Inversion.*" By WILLIAM EDWARD GARNER.

This model consists of a wooden ball, divided vertically into three equal sections, which are bolted together so as to leave a space between each. Additional stability is conferred on the structure by rings situated at the top and the bottom of the model. To each of the bolts, which are placed as near the centre of the model as possible, is attached a steel arm, capable of being vibrated with an upward and downward motion. The three arms are connected by thin cord to the middle of a central glass or metal rod DD′, which passes through the two rings. The method of attachment is seen by reference to the diagram (Fig. 2). By the movement of the central rod upwards through the rings, the three arms are caused to move simultaneously, and if this movement is made sufficiently great, they pass downwards into the enantiomorphous position.

The Werner model, constructed by the author (*Proc.*, 1912, xxviii., 65), was utilised to illustrate the change of maleic acid into fumaric acid, without the destruction of the double bond, and its employment in this connection naturally suggested its use in the transformation of *syn*-into *anti*-oximes. In the latter case the inter conversion of the isomeride may be demonstrated in either of two ways, namely, (1) by the inversion of the valencies of the carbon atom, and (2) by the inversion of those of the nitrogen atom. If both the carbon and nitrogen atoms undergo inversion, no change in the oxime is produced. The three cases are illustrated below:—

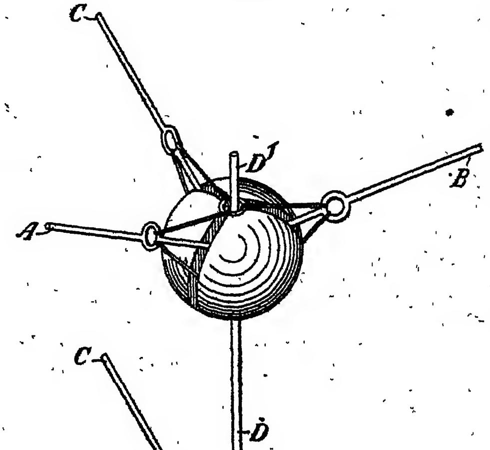
1.
2.
3.



The first method was easily carried out by means of the previously described model (*loc. cit.*), but in order to illustrate the second case it was necessary to devise a tervalent nitrogen model, the valencies of which could readily be inverted. The new model was constructed for this purpose (a model was first constructed in April, 1912). The central rod is then made of glass, and the valency arms, A, B, and C, represent the nitrogen tetrahedron of Hantzsch and Werner. Two of the valencies of this model are connected by thin rubber tubing to two arms of a carbon model, and the transformation effected, as has been previously described in the case of maleic and fumaric acids (*loc. cit.*).

The appearance of the nitrogen model, when completed, suggested to the author that it might be applied to represent some of the properties of the asymmetric carbo atom; the ends A, B, and C of the three arms, togethe with the end of the rod D, form the vertices of a tetra hedron, and consequently may represent the four group attached to a carbon atom. The ease with which th tetrahedron is inverted renders the model suitable for th illustration of racemisation and Walden inversio

FIG. 1.



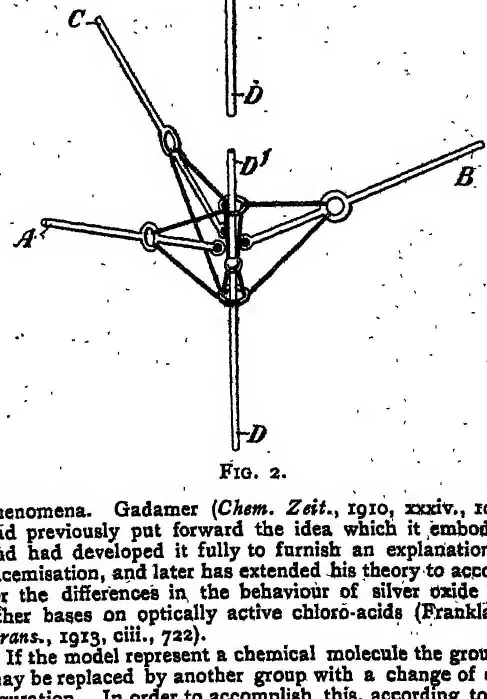
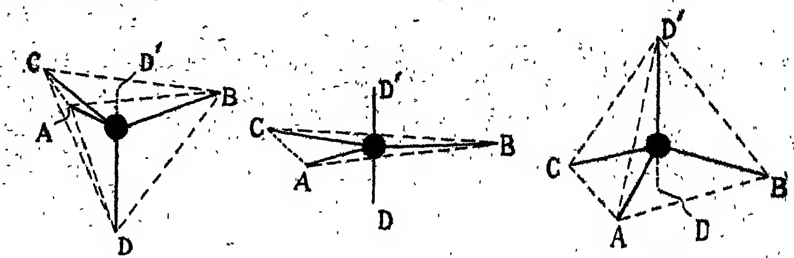


FIG. 2.

phenomena. Gadamer (*Chem. Zeit.*, 1910, xxxiv., 1004) had previously put forward the idea which it embodies, and had developed it fully to furnish an explanation of racemisation, and later has extended his theory to account for the differences in the behaviour of silver oxide and other bases on optically active chloro-acids (Frankland, *Trans.*, 1913, ciii., 722).

If the model represent a chemical molecule the group D may be replaced by another group with a change of configuration. In order to accomplish this, according to the Werner theory (*Ber.*, 1911, xliv., 881), the entering group must approach the molecule A, B, C, D from the side opposite to that occupied by the group D, and attach itself by means of its partial valencies at D′; if it is attracted to any of the other faces, no inversion would be obtained. Simultaneously with this addition, the group at D is gradually removed, and a corresponding movement of the other valencies occurs in a downward direction. The molecule will pass through an intermediate position II., in which the three valencies A, B, and C lie in one plane, and the fourth valency is divided into two halves at D and D′, and in this position the entering and extruded groups are attached to the carbon atom with equal force. In other intermediate positions the length of the central valency above and below the ball will indicate the relative strength of the attachment of the two groups. Finally, the groups



I. II. III.

pass into the enantiomorphous position III., in which the group, originally attached at D, is completely removed.

Coloured balls or paper may be attached to the arms to represent the various groups.

(We are indebted to the Chemical Society for permission to use the woodcuts illustrating this Paper).

188. "*The Baly-Krulla Theory of Fluorescence. A Reply to A. W. Macbeth.*" By Edward Charles Cyril Baly.

In a recent paper (*Proc.*, 1912, xxviii., 271) A. W. Macbeth criticised the theory of fluorescence which Dr. Krulla and the author advanced (*Trans.*, 1912, ci., 1469). It seems that this criticism is based upon a misconception of the theory itself and of the processes which take place.

According to the theory the condensed force fields surrounding the molecules of a substance may be opened up in stages by the influence of a solvent and of light. These stages may be called 1, 2, 3, 4, &c., and each one absorbs light of different wave-lengths, λ_2, λ_3, λ_4, &c. Whereas previously only two of these stages had been recognised, the existence of several definite stages in the opening up of the condensed field of force has now been proved, and it is hoped very shortly to communicate the results of certain observations, which clearly show how by the use of suitable solvents several different stages can be produced absorbing different wave-lengths of light.

Now it is obvious that in the absorption of these light waves considerable damping must be present. If this were not so it is evident that the whole substance would on prolonged exposure become diactinic. This is, however, absurd; owing to the damping that is present the light actually does work against the chemical forces, and is therefore changed, probably into heat, so that as the result a continuous and constant absorption of the light takes place. It would seem that Macbeth has not taken this damping into consideration. He states that if the substance can exist in stages 1, 2, 3, &c., these forms must be in equilibrium with one another. This is not a correct assumption. If the stage 3 were present in equilibrium with 1 and 2, and if, according to hypothesis, $1 \rightarrow 3$ or $2 \rightarrow 3$ can be produced by absorption of light λ_3, it is absolutely certain that λ_3 would be absorbed out of a light source containing these waves. It is an experimental fact that λ_3 is not selectively absorbed as long as the solvent necessary is absent. In other words, if a fluorescent material which absorbs λ_2 and emits λ_3 is screened from λ_2 no trace of selective absorption of λ_3 can be detected. This rules out of court the assumption that stage 3 is normally present in simple equilibrium with 1 and 2.

Under the influence of the light a photodynamic equilibrium is set up, which is a very different thing from the chemical equilibrium assumed by Macbeth.

Macbeth's first criticism therefore seems absolutely to fail; first, because he assumes that stages 1, 2, 3 are in simple equilibrium; secondly, because he neglected the damping; and thirdly, because he assumes that the substance when screened from λ_2 must absorb λ_3.

Macbeth states further that the theory, although it cannot explain fluorescence, is more capable of explaining phosphorescence. It is now generally agreed that the two phenomena are really the same, and only differ in the relative velocity of the two processes, absorption and emission. In any case of fluorescence or phosphorescence there are two processes: the absorption of energy and the emission of energy. If the velocity of the second process is equal to or greater than that of the first, then the substance fluoresces, but if the velocity of the emission is slower than that of the first, then phosphorescence takes place, namely, the persistence of the emission for an appreciable time after the exciting cause has been removed. In certain cases the velocity of the emission of the energy is exceedingly small, and in these circumstances the energy absorbed in the first process remains stored up in the substance for a very long time unless the velocity of the emission is increased by some means, such as the application of heat, when the phenomenon is known as thermoluminescence. There seems, indeed, no reason to assume any difference between the two phenomena, and if a theory can explain one of them, it follows that it can explain the other.

According to the theory, the stages 1, 2, 3, . . . *n*, inasmuch as they are stages in the opening up of the condensed system of a single molecule, are intimately connected with one another, and although the process by which λ_2 is absorbed in the solvent is the only one which light itself is capable of bringing about, yet there can hardly be any objection to the probability that the disturbance to the whole system produced in this way will bring the next possible vibration periods into play, namely, stage 3 followed in less degree by stage 4, and so on.

It is known that, given the necessary external conditions, stages 3, 4, &c., are characterised by vibrations synchronous with wave-lengths λ_3, λ_4, &c.; if these vibrations are brought into play by means of some other vibration they will emit light of the same wave-length.

Macbeth seems to have fallen into an error as regards the relationship between the wave-length of the exciting light and the emitted light. In producing phosphorescence of wave-length λ_3, λ_3 is not absorbed.

There does not seem to be any difficulty in reconciling all observations as regards the relations between temperature and phosphorescence. In the first place, the conditions may occur when the process $2 \rightarrow 1$ is very slow indeed, with the result that the process $1 \rightarrow 2$ will take place with absorption of λ_2. After some time the whole system will have absorbed considerable energy. On heating the system, or in many cases simply by rubbing or shaking, conditions are produced that enable the process $2 \rightarrow 1$ to take place, with the result that a considerable amount of free energy escapes as heat, and the whole system gets disturbed, and some of the vibrations of stage 3 are called into play with emission of λ_3. In this process no λ_2 is emitted. Care must be taken not to look upon processes $1 \rightarrow 2$, $2 \rightarrow 3$, or $1 \rightarrow 3$ as being directly reversible, absorbing or emitting the same amount of light energy, for if this were so, it would simply resolve itself into a case of resonance phenomena. Macbeth has fallen into error here when he says that the reverse process $2 \rightarrow 1$ will be accompanied by the emission of light λ_2, as demanded by Kirchhoff's law. Kirchhoff's law has nothing whatever to do with the case, for it is not a case of black body radiation. The reverse process $2 \rightarrow 1$ is not accompanied by emission of λ_2, but probably by emission of heat, and the process is not reversible.

The next point is: Why do some substances fluoresce only at low temperatures when the free energy is less than before? The lowering of temperature will tend to produce a more completely closed system of force lines round the molecule. There must naturally exist a particular condition of this condensing together of the force lines for the particular type of fluorescence observed to take place, and it follows directly from the theory that this condition may be produced at low temperatures when it does not exist at higher temperatures.

It has been shown (*Trans.*, 1913, ciii., 91) that when a substance is opened up by a solvent and by light, the amount of light absorbed increases with the dilution up to a maximum, after which further dilution tends to decrease the amount absorbed, which is then followed by the disappearance of the selective absorption. There is thus an optimum condition of concentration as far as absorption of light is concerned. This agrees with and explains Lenard and Klatt's and Urbain's observations on phosphorescence, for these authors have clearly shown that there is always a definite condition of concentration of phosphorescence in the diluent at which an optimum of phosphorescence is observed. Clearly at this concentration the phosphorogen has its closed force field just sufficiently opened up, and in that condition best adapted to respond to the exciting vibrations in such a way that the next stages, 3, 4, 5, &c., are called into play. This optimum condition only refers to one particular temperature. At a much lower temperature that condition will not necessarily give the optimum, and indeed, perhaps, may not give any phosphorescence at all. Some other concentration will be more suited for the new temperature conditions, and whilst this new concentration may not suit the old temperature, yet on cooling, the phosphorescence or fluorescence makes its appearance.

A specific example may make this clearer, namely, the phosphorescence of strontium sulphide. Becquerel (*Ann. Chim. Phys.*, 1859, [3], lv., 5) found that this material gives at 200° an orange phosphorescence, and as the temperature falls the colour passes through yellow, green, and blue until at −20° it is dark violet. This observation has been confirmed for a great number of substances by Lenard and Klatt (*Ann. Physik.*, 1904, [4], xv., 225, 425, 633). The reason of this effect is that the phosphorescent spectrum consists of at least five separate maxima having the above colours, and as the temperature is changed the relative intensity of the various maxima alters, and in the case of the strontium sulphide the tendency, with decrease of temperature, is for the maximum of the phosphorescence to move towards the shorter wave-lengths. If the separate bands in the phosphorescent spectrum be called A, B, C, D, E, then at the higher temperatures A will be the most intense, and as the temperature falls, B, C, D, E, in turn, show the greatest intensity. Each of these corresponds with a definite stage in the opening-up process, and the optimum condition for each stage, provided that the quantity of diluent remains the same, depends on the temperature. By varying the conditions of diluent, similar variations in the relations between the intensities of the different phosphorescent maxima can also be obtained under constant temperature conditions.

This fact has an important bearing on the general theory. Since the whole phenomenon of phosphorescence is a property of diluted matter, and since the fall of temperature allows more and more free energy to escape from the system, it follows that the lower the temperature the less is the phosphorogen opened up by the diluent. The observations on phosphorescence therefore run *pari passu* with the observations on absorption, for here the more a compound is opened up by a solvent the nearer the absorption maximum lies to the red. In other words, the more complex the solvent-solute system, or, speaking generally, the more complex the system of the force field dealt with, the nearer to the red will be its absorption and also its phosphorescent or fluorescent maximum. Macbeth in his criticism, based on the fact that some substances do not phosphoresce or fluoresce at ordinary temperatures and do so at low temperatures, has really advanced observations which strengthen and confirm the theory.

Again, Macbeth attempts to draw an analogy between a spring in various stages of compression and the stages 1, 2, 3, &c. This analogy fails absolutely from the start, because it requires the same energy in different amounts to obtain the spring in the different stages of compression, while in the real case the stages 2 and 3, &c., require for their actual production not only a different solvent, but light of different wave-length. He also contradicts himself here, because in order for the analogy to be complete from his point of view, the states of the spring when in different stages of compression must be in equilibrium with one another, an assumption he made for the stages 1, 2, 3, &c.

Two further criticisms of Macbeth still remain to be dealt with. First, Nichols and Merritt's observations that the position of maximum fluorescence is independent of the wave-length of the exciting light, and that the latter may be on the red side of the fluorescent maximum. Macbeth says the processes are now reversed, and λ_3 is being absorbed and λ_2 emitted. This is by no means the case. An inspection of the absorption and fluorescent curves shows that these extend considerably on each side of the maximum in each case. They frequently, indeed, overlap, and therefore the very fact of Nichols and Merritt's discovery strongly supports the theory. The shape of the fluorescent curve is characteristic of the substance under the conditions of solvent and concentration. This fluorescence will be produced by any wave-length included in the absorption band, even if it happens by chance to be longer than those emitted. The substance responds to and absorbs the longer the wave-length, and it is natural to expect that it would produce the same effect as any other wave-length in the same absorption band. Nichols and Merritt also observed in the same paper (*Physical Review*, 1904, xix., 18) that if the fluorescent substance has a second absorption band of longer wave-length than the fluorescent light, the absorption of light in this second region does not produce fluorescence, which fact, of course, is in agreement with this theory.

Finally, Macbeth quotes the observation of R. W. Wood, who showed that while fluorescing with light of definite wave-length a substance exerts no increased absorption of that light. On a theory of optical resonance "fluorescence absorption" might be expected, and the fact that it has been proved absent argues strongly against any simple resonance as a basis of fluorescence and absorption. Nothing whatever in the theory makes it probable that fluorescence absorption should take place. A criticism based on the fact that it does not take place seems therefore somewhat irrelevant.

The general conception may be made clearer by considering it in the following way:—Light energy (λ_2) is absorbed and converted partly into heat and partly into light energy (λ_3). In ordinary circumstances this reaction is not reversible, because λ_3 is not absorbed, but it might be considered that under certain special labile conditions it does become reversible. The absorption of λ_3 during fluorescence would mean that the same reaction was taking place in opposite directions at the same time, and absorbing energy on both counts. Whether the process is reversible or non-reversible, there is no reason why λ_3 should be absorbed during fluorescence.

PHYSICAL SOCIETY.

Ordinary Meeting, June 13th, 1913.

Prof. C. H. LEES, F.R.S., Vice-President, in the Chair.

A PAPER on "*Some Experiments on Tinfoil Contact with Dielectrics*" was read by Mr. G. E. BAIRSTO.

This paper describes some experiments showing how the accuracy of the different kinds of electrical measurements

that are made on condensers is influenced by the use of an imperfect tinfoil contact.

1. In connection with the measurement of the direct-current conductivity of a condenser having tinfoil armatures, the experiments of Mr. Appleyard (*Proc. Phys. Soc.*, 1905, xix., 724), in which the current a minute or two after the first switching on of the current was greater than that at the time of switching on, are referred to. These experiments go into the matter in more detail. By choosing a suitable dielectric—celluloid, which has a conduction current of a greater value than the rate of change of displacement current—it was found possible to greatly increase the magnitude of these secondary increases in current.

At very low pressures there is very little increase of current, and moreover what little increase there is over in a few minutes, but as the pressure is increased the secondary increase gradually becomes larger and takes longer to attain its maximum value. The maximum effect was reached at about 750 grms./sq. cm., when the increase of current amounted to 40 per cent, and the time required five and a-half hours. At very large pressures, when the contact becomes an intimate one, the increase of current becomes smaller again and the time required also smaller.

If the pressure is left on and the voltage removed for some hours a repeat test follows the same course, the current starting at the same value and attaining the same maximum value. Voltage has, therefore, quite as much effect as pressure in bringing about an intimate contact, and acts independently of it.

By considering the geometry of the tinfoil humps, an explanation of these various effects is given, and the different ways in which the pressure and the voltage increase the degree of contact between the dielectric and the tinfoil armatures are described.

2. While considerable errors are liable to be made in deducing the specific direct current conductivity of a dielectric between tinfoil armatures, the same is not true for measurements of the alternating-current conductivity. The influence of the bad contact is twofold. Firstly, it decreases the apparent capacity by inserting in series with the condenser under test a very large but still finite air condenser. This causes a decrease in the measured conductance. Secondly, because of the decrease in area of contact, it decreases the magnitude of that component of the conductivity which is independent of the frequency—*i.e.*, the purely ohmic conductivity.

By considering the system as equivalent to a leaky condenser in series with a very large capacity due to the air film, expressions are deduced for the equivalent capacity, conductance, and power factor, and these expressions furnish us with the means of separating out the two above effects.

It is shown experimentally, even under the worst possible circumstances, the dielectric being only lightly bound up with the interleaved tinfoil, that for telephonic frequencies the maximum difference between the observed conductivity and true conductivity is 15 per cent and of capacity is 5 per cent. With the condenser tightly bound with tape and wedges of wood inserted, the maximum difference was only 4·5 per cent in the conductivity and 2·5 per cent in the capacity.

3. Finally, the influence of imperfect contact upon the accumulation of residual charge is considered. It is shown that if we have a condenser with tinfoil armatures, as, for instance, tn the Franklin jar, with its rigid metallic coatings, the recovery of a residual charge is obscured by the presence of creeping surface charges coming out of the undischarged portions of the dielectric leading to an apparent residual charge much more than the true residual charge left in the dielectric.

Dr. J. A. Fleming thought the paper contained much valuable information. He emphasised the difficulty and importance of getting rid of the air film. For many dielectrics, such as glass or indiarubber, pressure could not be applied. The tinfoil could be squeegeed on to the dielectric when the condenser was made, or the condenser could be put in a vacuum subsequently. For a constant condenser it was also necessary that there should be no chemical action between the metal plates and the dielectric such as occurred, for instance, in the case of copper foil and celluloid. He thought Mr. Bairsto's experiments on residual charges were very interesting. Theorists had attributed the whole effect to the properties of the dielectric, not to the bad contact between it and the electrodes. The paper was also useful in pointing out the pitfalls of experimental work on the subject.

Mr. R. Appleyard was glad Mr. Bairsto had adopted the direct reading method of examining the changes in dielectric resistance. The author had kept the current on till a steady deflection had been obtained. It was often more valuable to take the reading after a definite time, say, one minute. He did not think that the alternating current test in the second part of the paper had much bearing on the first part. The work on the residual charge was most interesting.

Mr. E. H. Rayner remarked that it was assumed by all workers on the subject that the properties of the dielectric itself were not directly influenced by pressure, whereas this might in itself decrease the resistance of the dielectric. He would like the author to carry out pressure experiments on a silvered celluloid condenser.

Dr. A. Russell agreed with the last speaker. Celluloid was far from homogeneous. The dielectric resistance was not a constant, but was a function of the applied voltage.

Mr. G. L. Addenbrooke emphasised the effect of heating of the dielectric due to the energy loss in it. He also remarked that the author had neglected surface conduction.

Mr. W. Duddell remarked that the paper showed the importance of a thin air film in the determination of the conductivity and capacity of a condenser. For standard condensers makers knew that if the air was not excluded the capacity would not remain constant. If a high voltage were applied to such a condenser and left on for some time the capacity afterwards would be found to be permanently altered. Even with as low a voltage as 200 volts we may get brush discharges into the air film.

Prof. C. H. Lees expressed his interest in the third section. He would like to know whether tinfoil electrodes under pressure would give the same residual discharge curve as mercury electrodes.

The Author, in reply to Prof. Lees, was sure it would give the same curve.

A paper "*On a Method of Measuring the Pressure of Radiation by means of Thin Metal Foil*" was read by Mr. Gilbert D. West.

The pressure of the radiation emitted by a carbon filamentl amp at a distance of a few centimetres is sufficient to cause a microscopically measurable deflection of the end of a suspended strip of gold or aluminium foil, and by this means the radiation pressure can be calculated knowing the weight of the strip. The results agree to within about 10 per cent with the energy content per cubic centimetre as measured by the initial rate of rise of temperature of a copper plate exposed to the radiation.

The best results are obtained by working in an atmosphere of hydrogen, 1 cm. to 2 cm. pressure, but good results are obtained with hydrogen at atmospheric pressure. Air at 1 cm. to 2 cm. pressure also gives good results.

The method involves no laborious adjustments, and the apparatus is not seriously affected by vibration.

Prof. C. H. Lees remarked that the point in the above paper was its extreme simplicity.

Dr. C. W. C. Barlow (in some remarks communicated by Prof. Poynting) pointed out that the author ought to allow for the light reflected from the foil to the glass wall and back again to the foil. This would improve the agreement in the author's measurements.

A paper "*On the Emission of Electricity from Hot Bodies and the Quantum Theory*" was read by Dr. W. WILSON.

The paper gives a theory of the emission of electricity from hot bodies which is based on the quantum theory of energy. A formula connecting the thermionic current and the temperature of the emitting body is deduced. This formula closely resembles that of Richardson, and agrees slightly better with experimental results.

Prof. J. W. NICHOLSON thought the paper was a valuable one in that it connected up yet another phenomenon with Planck's quantum theory of radiation. It was probable that Planck's constant h was in some way an electron constant, and that the emission of energy was discontinuous because emission of electrons was discontinuous.

NOTICES OF BOOKS.

Metallic Alloys. By G. H. GULLIVER, B.Sc., F.R.S.E., A.M.I.Mech.E., M.Inst.M. Second Edition. London: Charles Griffin and Co., Ltd. 1913.

THE text of this book is based upon various courses of lectures on alloys given by the author at the University of Edinburgh and at the Heriot Watt College, Edinburgh. It gives a systematic and thoroughly scientific view of the structure and constitution of binary and tertiary alloys, as well as a short account of the methods of investigation employed, and of the use of the microscope in general engineering practice. The second edition has been very greatly enlarged, and many new microphotographs and equilibrium diagrams have been added, so that the illustrations now number over 300, while the references to current literature are almost as numerous.

Organic Chemistry. By HOWARD D. HASKINS, A.B., M.D. Second Edition. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1913.

A COMPLETE survey of the facts of organic and physical chemistry which have an important bearing upon medical science is to be found in this book. The author has endeavoured to give a short description of every compound which should be known to the medical student, and the principles of physical chemistry are outlined. A course of practical work is described, including preparations, tests for purity, and methods of identification. A special feature of the text is the great number of structural formulæ given, with which the student is recommended to make himself thoroughly familiar.

Nitrogenous Soil Constituents and their Bearing on Soil Fertility. By OSWALD SCHREINER and J. J. SKINNER. Washington: Government Printing Office. 1912.

THIS Bulletin contains a detailed account of the effect on seedlings of the different nitrogenous soil constituents. The investigation proves that some compounds are beneficial, while others, which appear to occur normally in soils, are harmful. Thus picoline carboxyllic acid retards growth, and guanidine produces effects similar to those due to disease. All the culture experiments were carried out under strict chemical control, so that all possibility of the interference of bacterial influences was excluded. The Bulletin contains a complete summary of the effects of organic compounds of all classes upon the growth of various plants, including the results of many tests carried out in previous researches.

Observaciones sobre el Método Crioscópico y Relaciones entre los Cuerpos Simples. ("Notes on the Cryoscopic Method and Relations between Simple Substances"). By CARLOS E. HEREDIA. Buenos Aires: A. Guidi Buffarini.

IN the first part of this thesis the results of many cryoscopic experiments are given, and some general inferences made from them; for example, the author has drawn attention to the fact that the maximum temperature of solidification is not necessarily equal to that of fusion. In the second part the question of the constitution of the elements is discussed and fundamental laws are formulated, showing how the chemical and physical nature of an element and also its type are functions of the atomic constitution which is a variable depending upon the degree of condensation of the atoms. The author expounds at length and with great intrepidity his views on force, energy, and matter, but does not appear to have made any material contribution towards the solution of the problem of their natures.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Academie des Sciences. Vol. clvi., No. 14, April 7, 1913.

Dehydration and Decomposition of Hydrates of Uranyl Nitrate.—M. de Forcrand.—When uranyl nitrate hexahydrate is dehydrated in the cold at atmospheric pressure two phases may be distinguished. During the first four or five days there is a tendency to form the trihydrate, and then when it is formed the loss of water becomes much slower, and stops completely when the dihydrate is reached. When the dihydrate is dehydrated at 98° in a current of CO_2 a monohydrate is formed, containing less than 1 per cent of uranic acid. A practically anhydrous salt can be obtained by dehydrating the dihydrate at 165° in a current of CO_2 containing nitrous vapours.

New Double Sulphate of Cerium and Silver.—Emm. Pozzi-Escot.—When a warm sulphuric acid solution of cerium sulphate is treated with a warm solution of silver nitrate an orange-yellow crystalline precipitate of a double salt is obtained. When it is washed and dried and the excess of sulphuric acid is removed by heating it to 400°, it is found that its composition corresponds to the formula $10Ce(SO_4)_2.6Ag_2.SO_4$. The anhydrous double salt is slightly soluble in cold water; when boiled with water it readily dissolves, undergoing decomposition.

Solubility of Thorium Oxalate.—A. Colani.—When thorium oxalate is dissolved in water containing at least 20 per cent of hydrochloric acid, chloro-oxalate is formed and oxalic acid is precipitated. The solubility of the oxalate in oxalic acid is less than in hydrochloric acid, and the solubility in the latter is greatly decreased by the presence of oxalic acid.

Action of Monosodium Acetylene on Alcoholic Iodides. Preparation of True Acetylenic Hydrocarbons.—Paul Lebeau and Marius Picon.—Chloride and iodide of methyl react at −50° on a solution of monosodium acetylene in liquid ammonia and allylene is obtained, $C_2HNa + CH_3I = NaI + CH_3.C{\equiv}CH$. The yield is about 96 per cent. Normal hexine can be prepared similarly from normal butyl iodide.

Catalytic Etherification in Dilute Solution. Preparation of Ethyl Acetate.—F. Bodroux.—The distillation of a mixture of acetic acid and propyl alcohol in presence of a concentrated aqueous solution of aluminium iodide leads to the formation of a large quantity of propyl acetate, and the production of this ether salt can only be attributed to the catalytic action of the dissolved salt. Ethyl acetate can be obtained from a mixture of ethyl alcohol and acetic acid if an aqueous solution of sulphuric acid is used as catalyst, and the proportion of organic acid etherified is greater the greater the concentration of the sulphuric acid in the aqueous solution.

No. 15, April 14, 1913.

Reduction of Magnesia by Aluminium.—Camille Matignon.—To reduce magnesia an intimate mixture is made with aluminium powder, which has been freed from fat by repeated washings with benzine and ether, in the

proportion of MgO to $\frac{1}{2}Al_2$. The mixture is pressed into tablets, and heated in an exhausted steel tube in a porcelain tube. At 1200° the magnesia is reduced and the magnesium is deposited in large crystals on the cooler part of the tube. The reduction is practically complete and constitutes a useful method of preparing magnesium.

Formation of Humic Matter by the Action of Polypeptides upon Sugars.—L. C. Maillard.—The author has already shown that humic matter can be prepared by the action of amino acids upon reducing sugars. The reaction is due to the groups NH_2 and COOH, and is shared by the polypeptides, which contain the same groups. Thus the behaviour of glycyl-glycine exactly resembles that of glycocoll.

Bulletin de la Société Chimique de France.
Vol. xiii.-xiv., No. 8, 1913.

Solution of Constituents of Alluvial Sand by Subterranean Water.—F. Dienert.—When rain-water penetrates into sand in presence of carbon dioxide it dissolves calcium carbonate, magnesia, silica, and alkaline salts in definite proportions. But it has been shown that if the water circulates in sands in presence of an insufficient quantity of carbon dioxide it loses chiefly calcium carbonate, very little magnesia, no iron, aluminium, silicon, or alkaline salts.

Colour Reaction for Detection of Hyposulphites.—Emm. Pozzi-Escot.—To test for hyposulphite in a solution an equal volume of 10 per cent ammonium molybdate is added, and 5 cc. of pure concentrated sulphuric acid are run in by means of a pipette. In presence of hyposulphite a blue coloration is produced at the zone of separation of the aqueous mixture and the acid. If the concentration of the hyposulphite solution is greater than 1/5000, the blue zone is preceded by a more or less yellowish green zone. It is possible by means of this reaction to detect the presence of 0·00005 grm. of sodium hyposulphite.

Determination of Iodine in Iodotannic Syrup.—Emm. Pozzi-Escot.—A simple and rapid method of determining iodine in iodotannic syrup is as follows:—Twenty-five cc. of the syrup are diluted with 50 cc. of water. Ten cc. of chloroform or carbon disulphide are added, then 2 cc. of concentrated sulphuric acid and an excess of a saturated solution of potassium permanganate. The iodine is thus liberated, and dissolves in the organic solvent, and may be determined by means of a titrated solution of sodium hyposulphite.

Solubility of Certain Metallic Salts of Volatile Fatty Acids in Organic Solvents.—Henri Agulhon.—If the copper salt of an organic acid is produced in an aqueous medium by double decomposition, and the liquid is then shaken with certain organic solvents, the latter in certain cases extract all or part of the copper salt formed. The amount extracted is a function of the molecular weight of the acid used. Thus, whatever the solvent none of the salt is extracted in the case of formic or acetic acids. With propionate a light blue coloration appears in acetic ether, the aqueous solution remaining deeply coloured. In the case of butyrate an intense blue coloration is produced with acetic ether, ether, chloroform, amyl alcohol, while the aqueous solution becomes colourless.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xlvi., No. 6.

Vapour Pressure of Liquid Tin Amalgams containing Small Amounts of Mercury.—A. Sieverts and H. Oehme.—The vapour pressures of liquid tin amalgams containing from 0·8 to 8 per cent of mercury are nearly proportional to the concentration of the dissolved mercury between 300° and 360°, and for pressures from 2—70 mm. Hg. Two single series of experiments with 2 and 10 per cent Hg gave the same result for 515° and 528°, and a pressure interval of 173—886 mm. Hg. Thus the solution of monatomic mercury vapour in liquid tin follows Henry's Law, while in the solution of diatomic gases in metals the quantity dissolved is proportional to the square root of the gas pressure.

Aromatic Telluretin Compounds.—Karl Lederer.—The methyl ether of bromacetic acid unites with diphenyl telluride to give a stable compound of formula $(C_6H_5)_2TeBr.CH_2.COOCH_3$, corresponding to the sulphur compound $(CH_3)_2SBrCH_2.COOH$. The bromine atom can be replaced by chlorine, and a picrate of similar composition can be obtained. The ethyl ether of bromacetic acid also combines with diphenyl telluride, but the compound formed is less stable than the methyl compound. When silver oxide acts on the ester of diphenyl telluretin bromide the bromine atom is replaced by hydroxyl and the ester is saponified.

Tetraphosphorus Trisulphide and a new Phosphorus Oxy-sulphide, $P_4S_3O_4$.—Alfred Stock and Kurt Friederici.—Tetraphosphorus trisulphide is very stable in absence of air and moisture when the temperature is raised, and solid P_4S_3 is very stable towards air. When oxygen is led through a solution of P_4S_3 in carbon disulphide in absence of moisure a new oxidation product, $P_4S_3O_4$, is obtained. It is a yellowish white heavy powder which decomposes when heated. It is very readily attacked by water, and gives a yellow solution with caustic soda. When ozone acts on P_4S_3 solutions, higher oxidation products are obtained. These resemble $P_4S_3O_4$ in their behaviour, but give a colourless solution with caustic soda.

MISCELLANEOUS.

Royal Society of Arts.—The Annual Meeting of the Royal Society of Arts was held on Wednesday, June 25th, Lord Sanderson, G.C.B. (Chairman of the Council), in the Chair. The usual Report recording the Proceedings of the Society during the past year was read. H.R.H. the Duke of Connaught was re-elected President, with the usual number of Vice-Presidents and Council. Thirty-five new Members were elected, making a total of 238 elected during the Session, the 159th of the Society.

Royal Society of Arts.—Award of Medals.—The Council of the Royal Society of Arts have awarded the Society's Silver Medal to the following readers of papers during the Session 1912—13:—

Dr. F. Mollwo Perkin—"Natural and Synthetic Rubber."
Joseph Pennell—"The Pictorial Possibilities of Work."
Henry J. Wilson—"The Education and Employment of the Blind."
E. Russell Burdon, M.A.—"The Development of Research Work in Forest Products."
Frank Bailey, M.Inst.C.E.—"Electric Supply in London."
Walter C. Hancock, B.A., F.I.C.—"The Physical Properties of Clay."
H. V. Lanchester, F.R.I.B.A.—"The Design and Architectural Treatment of the Shop."
F. G. Ogilvie, C.B., LL.D.—"The Science Museum."
Axel Welin, A.I.N.A.—"Life-saving at Sea."
Sir Bradford Leslie, K.C.I.E., M.Inst.C.E.—"Delhi, the Metropolis of India."
J. Forrest Brunton—"The City of Karachi."
N. G. Cholmeley, C.S.I., late Commissioner, Magwe Division, Burma—"The Oil-Fields of Burma."
Sir John Benton, K.C.I.E.—"Irrigation Works in India."
W. H. Warren, LL.D., M.Inst.C.E., M.Am.Soc.C.E., Dean of Faculty of Science and Challis Professor of Engineering, University of Sydney—"The Hardwood Timbers of New South Wales."
C. E. W. Bean, M.A., B.C.L.—"The Wool Industry in the British Dominions."
The Right Hon. Sir Joseph George Ward, Bart., K.C.M.G., LL.D.—"New Zealand: an Ideal Place of Residence."

THE CHEMICAL NEWS.

VOL. CVIII., No. 2798.

ACTION OF SEA-WATER ON FLANGES USED IN MARINE ENGINEERING.

By SERGIUS KERN, M.E., St. Petersburg.

BRONZE flanges used in marine engineering were placed in sea-water (Atlantic Ocean composition) for a period of two months. Before suspending them in a wooden box, by ropes, they were turned and polished.

Composition of Flanges.

	Cu (per cent).	Sn (per cent).	Zn (per cent).
1.	90·0	3·5	6·5
2.	89·5	4·5	6·0
3.	87·0	8·0	5·0
4.	88·0	10·0	2·0

Weight of Flanges before Immersion.

	Pounds.
1.	27·73
2.	27·82
3.	27·48
4.	27·55

After two months the flanges were taken out of the bath of sea-water. On the surface they were bright; only here and there a small film of Cu_2O was observed.

Weight of Flanges after Immersion.

	Pounds.
1.	27·70
2.	27·79
3.	27·45
4.	27·51

The mechanical tests of test-pieces, cast with the flanges, were as follow:—

	Breaking strain. Tons per sq. in.	Elongation in 2 in. Per cent.
1.	15·15	34
2.	15·68	28
3.	15·77	31
4.	15·04	18

These experiments were made in order to show that the flange alloy No. 2, which was found by us to be the best for brazing purposes, corrodes not more than flange-alloys Nos. 3 and 4, prescribed by the Russian marine authorities.

Precipitation of Aluminium Hydroxide by Bromine from Aluminate Solutions.—W. Jakób. Bromine precipitates pure aluminium hydroxide from a boiling alkaline aluminate solution, and the reaction is quantitative and can be used to separate aluminium from chromium. The solution containing the two metals must first be treated with sodium hydroxide solution, drop by drop, till the precipitate dissolves. Then bromine water is added to the cold solution till the green colour is replaced by yellow. The solution is boiled and the aluminium hydroxide separates in a compact form. To remove the last traces of chromium from the precipitate the liquid is decanted off, and the precipitate is treated with water containing ammonia and ammonium nitrate, boiled for a few minutes, and filtered off. The small quantities of precipitate clinging to the walls of the flask are separated by means of dilute nitric acid, and added to the main bulk after neutralisation with ammonia. The method is not suitable for the precipitation of aluminium hydroxide in presence of sulphuric or boric acids.—*Anzeiger der Akademie der Wissenschaften in Krakau*, 1913, I. A.

ESTIMATING THE QUALITY OF PAPER.*

THE MICROSCOPICAL, PHYSICAL, AND CHEMICAL TESTS OF THE UNITED STATES BUREAU OF STANDARDS.

IT is a well recognised fact that an accurate knowledge as to the materials and chemicals entering into the composition of a paper is of great value to every paper maker who may be called upon to match a given sample. Manufacturers at present must depend on their personal judgment for such information, and the ability to correctly judge papers may only be acquired by long years of experience. To such an experienced man the first look at a particular sheet of paper reveals the general class to which it belongs, whether writing, printing, wrapping, board, &c. A second glance reveals the relative grade into which the particular class is subdivided. This preliminary information at once brings to the mind of the experienced man a picture of the general process of manufacture required to produce such a paper. By the use of his sense of smell he, in many cases, is able to determine whether it is animal sized or not; he presses his tongue against the sheet and says whether it is "water-leaf" or "sized" paper, and whether "slack," "medium," or "hard" sized; if a coated paper his tongue will indicate it. Upon closer inspection and a liberal use of the sense of "sight" and "touch," he is able to estimate the weight per ream, the thickness of the sheet, the fibre composition, and general method of treatment in the beater room, on the machine, and in the finishing room. He may also be able to give an estimate of bursting strength and general folding quality. The result of this method of testing is only comparative, and therefore lacks fundamental necessity of numerical expression for record purposes.

At the present time there is developing, both within and without the paper trade, a growing interest in the subject of paper testing. There is a demand on the part of the buyer for better methods to enable him to determine the quality of a paper. That there is this growing interest in the subject and a general demand for standard methods of testing is most conclusively shown by the work which is being accomplished in the commercial paper testing laboratories that are starting up in various parts of the country.

This increasing general interest in paper testing has been the cause of developing a series of tests that apply both to the physical and chemical properties of a paper. These tests are not meant to give absolute values, but if due care is exercised in the selection of a representative sample and in making the necessary tests, then numerical values will be obtained which to a large degree indicate something of the quality of a paper. Such a method offers the only means whereby a record of a paper may be kept.

In this discussion of paper testing, it should be distinctly understood that these tests do not cover every quality of property a paper may have. The degree with which one sample is a colour match for a second sample must depend upon the ability of the eye of the individual. The matter of "finish" is a second property, which so far cannot be expressed numerically, and for which there are no physical tests. The degree with which one sample conforms to another in finish is purely a personal element, and depends upon the experience of the individual.

At the present time there are no physical methods by which an accurate comparison may be made to determine when a paper contains a larger amount of dirt than is acceptable, or just what degree of "wild formation" shall render a paper non-acceptable. These two properties of "dirt" and "formation" are left to the judgment of the individual, and depend on a hazy mental idea of what he individually believes to be a point beyond which a paper

* Paper read at a meeting held under the auspices of the Bureau of Standards at Washington, D.C., Jan. 13, 1913. From the *Chemical Engineer*, xvii., No. 2.

becomes undesirable for the particular purposes for which it was intended.

The laboratory testing of a sheet of paper then narrows itself down to determining those properties which have a nearly fixed value or may be expressed in definite numerical terms. These values are such that when due care is exercised two or more individuals using the same methods and samples and working independently will obtain duplicate results. In other words, such methods very largely eliminate the personal element of the individual wherever the properties of a paper may be given a numerical value.

The general examination of paper may be subdivided into three parts as follows:—

Microscopical examination.
Physical tests.
Chemical analysis.

A microscopical examination will disclose the kind or kinds of fibres from which a given paper was made, and the experienced man will with considerable accuracy be enabled to estimate the proportions of various kinds of fibres used. The microscope also helps to indicate how much a stock has been beaten.

The testing to determine the physical properties of a paper is divided into determining: weight per ream, thickness, bursting strength, tensile strength, folding endurance, expansion, and absorption.

The chemical analysis will disclose the amount of ash retained and the amount and kind of size used. A chemical examination will also give much information in regard to colours used. All of this information is of the utmost importance in determining the quality of a paper.

The principal purpose of a microscopical examination is to determine what fibre or fibres were used in making a paper, and then to estimate the relative proportion of each on a basis of 100 per cent for the total fibre composition. Such an examination requires the following apparatus:—beakers, test-tubes, slides for microscope, two long pointed steel dissecting needles, Bunsen burner, and tripod stand (or other means of heating sample), one large bottle of a ½ per cent solution of caustic soda, one small bottle of 25 per cent hydrochloric acid, six small dark coloured glass bottles, with dropping stoppers for stains, small pieces of filter paper, and a microscope which for ordinary work should be capable of magnifying about forty-five times. The binocular microscope will be found to be best suited for estimating work where it is desired to study the markings and special characteristics of a fibre, then a microscope capable of magnifying from 150 to 200 times should be used.

As all vegetable fibres are highly transparent and almost entirely colourless, when seen under the microscope, it is very necessary to use some staining solution to colour the fibre in order to bring out their size and shape and general markings. The best stain for this purpose is the so-called "Herzberg" stain, which is what is known as a selective stain, that is, it has the property of giving a yellow colour to most uncooked fibre, such as mechanical wood; chemical woodpulps are coloured in indigo blue; and cotton, linen, and some other fibres are coloured in wine red.

The staining solution is made up as follows:—

Solution A.

Zinc chloride	20 grms.
Water (preferably distilled)	10 cc.

Solution B.

Potassium iodide	2·1 grms.
Iodine crystals	0·1 grm.
Water (preferably distilled)	5·0 cc.

Dissolve A by adding the water to the zinc chloride in a glass beaker.

Dissolve B by adding a few drops of the water to the potassium iodide and iodine crystals in a glass beaker and after dissolving add the remainder of the 5 cc. of water.

The two solutions — A and B — are then mixed together and allowed to stand for twenty-four hours to settle, after which the clear liquid may be poured off and divided between two of the dark glass bottles with the dropping stoppers. All iodine solutions will fade in light, and should, therefore, be kept in the dark as much as possible.

It is a very good plan to use two more of the dropper stoppered bottles to keep a concentrated solution of zinc chloride and water in one and a concentrated solution of potassium iodide and iodine in water in the second; these two solutions will be found handy in adjusting the Herzberg stain.

The preparation of a sample of paper for the microscope is as follows:—Several small pieces of paper of about the area of a cent are cut from different parts of the sheet of paper; these pieces are then placed in a beaker and covered with ½ per cent caustic soda solution, the whole mass is then brought to boil over a suitable heating device. After boiling for about a minute, the liquid is poured off and some tap water added to wash out the caustic soda, and two or three drops of a 25 per cent hydrochloric acid solution added to neutralise the alkali.

The slightly acid solution is then poured off and enough of the small pieces of paper is pinched off and rolled into a ball of about the size of a pea. This small ball of pulp should be well rolled between the thumb and finger and then placed in a test-tube and the test tube about half filled with water. Care must be exercised to rinse the hands after working each sample, to keep from contaminating the sample following. The test-tube is then shaken vigorously until the paper has been entirely broken up and the fibres are well separated. A few fibres are next removed on the point of the microscope needle from the test-tube, and a small sample is placed on each end of one of the microscope slides. The slide should be held in the holder over some black surface, as it is a great help to the eye to look at the white fibres against a black background. The wet fibres on a slide may best be dried by covering them with good filter paper and left for a few minutes to dry in the air.

The fibres are thoroughly dried and a drop of the Herzberg stain is added, and then the fibres are well "teased" out by the use of two microscope needles, a cover-glass is placed upon the fibres and well pressed down, all the stain pressed out around the edges of the glass being removed with filter paper, and the slide polished with paper or cloth.

The slide is next placed under the microscope, and after studying the various fields an estimate of the proportion of each of the various kinds of fibres may be given.

It is best to use four stains for this work, that is, each stain is of slightly different strength, as each one gives the best results on certain fibres. For example, a stain that clearly brings out the wine-red colour on cotton and linen fabrics, as a rule, usually does not give the best blue colour on bleached soda and sulphite pulp; the same stain on ground woodpulp has almost no effect at all.

In making up a stain to produce the best colour on the particular fibre, the following points should be remembered:—

Two or three drops of water added to a good stain for rag and bleached chemical wood will tend to fade out the wine-red colour, the blue colour will remain nearly unchanged, and the yellow colour on ground wood will be brought out very much clearer. In other words, a good rag stain, when used on ground wood, produces almost no colouring of the ground wood fibres.

The addition of two or three drops from the bottle containing the concentrated solution of iodine and potassium iodide, in water, will produce a deeper wine-red on rag fibres, while the addition of a few drops of concentrated solution of zinc chloride in water will produce a deeper blue on chemical wood fibres.

It should be remembered that these iodine solutions

will continually fade out, and that the best results may only be obtained when the stains give the proper colours.

The easiest and best way in which to secure a stain of the right colouring capacity is to keep on hand the following pulps: Bleached soda and sulphite pulps, unbleached sulphite, ground wood, and beaten rag stock. The rag stock may most easily be secured by using a sheet of good quality of filter paper, which is always made from "all rag" stock. Now take small bits of the bleached soda and bleached sulphite pulp and thoroughly mix them, after first separating them in water in a test-tube. Place a small sample on a microscope slide, thoroughly dry the fibres, add one drop of stain, separate fibres with the needles, place cover glass in position, and place slide under microscope. Each fibre seen should be of a blue colour, the sulphite fibres appearing much wider and longer than soda fibres, and should show a lighter blue colour, as the fibre is more translucent than a soda fibre, while the soda fibre should take a darker blue colour.

Soda and sulphite fibres should show a slight colour difference, and soda fibres being coloured a darker indigo blue, while sulphite fibres should be coloured a lighter indigo blue. If this colour difference is not clearly brought out, then either water or zinc chloride solution should be added, depending on whether it is desired to weaken or deepen the colours.

Some rag fibres should now be added to the test-tube, and a second slide made up, using a bottle of stain which is intended to produce best results on mixture of rag and woodpulps. This second stain is adjusted by adding water, zinc chloride, or iodine-potassium-iodide, or all as may be needed, until the three fibres, soda, sulphite, and rag, are all clearly brought out.

A third stain should be prepared for such papers as may contain ground wood by using mixture of ground wood and unbleached sulphite, and then adjusting the stains to give the best colours. The proper yellow for ground wood is the lemon yellow, never an orange yellow, as then the sulphite pulp is too slightly coloured and ground wood estimates are necessarily too high.

The experienced man may by using this method get some very surprising results. The Bureau of Standards believes that in papers containing mixtures of rag and bleached chemical wood, a careful microscopical estimate is well within 5 per cent of the correct fibre contents. For papers containing ground wood, especially where the percentage of ground wood is high, then the degree of accuracy is within 10 per cent of the correct fibre contents.

For laboratory use, the quickest sheet weighing device is the quadrant paper scales, so graduated that the corresponding ream weight—either 500 or 480 sheets—is read off directly in pounds.

Thickness of a paper may best be determined by the use of a spring micrometer having a hand that travels around a circular dial. This dial is graduated into thousandths of an inch and may be read to ten thousandths. In using such a gauge care should be taken to see that the pressure on the paper is constant, and also that the pressure surfaces are large enough not to compress the paper.

The bursting strength of a paper is determined with a machine by which the paper is firmly clamped against a rubber diaphragm, through which the pressure is applied to a circular area of the paper measuring one square inch. The actual pressure of the liquid under the rubber diaphragm required to burst the paper is registered on a carefully calibrated pressure gauge, reading pounds per square inch. An average of ten readings is taken as the correct bursting strength.

The tensile strength of a paper is determined upon a suitable machine, capable of accurately recording the tension required to break a strip of paper, when held at each end by suitable clamps, and the clamps are moved apart until breaking of the paper occurs.

The folding endurance is measured on a machine in which a strip of paper of definite size is clamped. The clamps are held apart under definite tension and the paper is caused to bend back and forth upon itself until the fibres wear through at line of folding. The number of double folds is recorded automatically by a suitable device.

Expansion of a paper may be determined by submitting the paper to different atmospheric conditions and noting resultant size of sheet at each change in the atmosphere.

The measure of absorption of a paper is the height to which, in a given time, a liquid will rise by capillary action, when one end of a vertically held strip of paper is immersed in water. This test, as well as all physical tests, must be made under a uniform condition of humidity.

The work of the paper laboratory at the Bureau of Standards comprises the testing of papers for the government service and the general public; also a study of methods of paper manufacture for the purpose of obtaining information of value in the preparation of government paper specifications. Information thus obtained is also at the disposal of the general public who may be interested in selling or buying paper under definite requirements.

It is not the intention of this bureau to go into general commercial paper testing, for the reason that there are regular commercial laboratories that are well equipped to do this work. Tests in dispute between outside parties will be taken up as an absolutely disinterested referee; in such case the bureau will very willingly give all possible assistance.

The equipment of the paper laboratory is at the service of the paper manufacturer as well as the user of paper for the investigation of problems of wide general interest, and it is desired to impress upon the trade and the general public that they are always welcome to such information as we may possess, provided such information does not come to us in a confidential manner.

The United States Government throughout its various branches consumes 40,000,000 lbs. of paper each year. This large amount of paper includes almost every grade or kind on the American market. The acceptance or rejection of such a large and varied amount of paper necessarily involves good judgment on the part of the paper inspector, together with an intimate knowledge of the manufacture of all kinds of paper, and a knowledge of the various uses to which each grade may be put. Is it reasonable to expect to find one or even two men who combine such a knowledge?

It is the firm belief of the Bureau of Standards that all manufacturers and users of paper will readily recognise that a correct set of definite chemical and physical tests, when carried out under uniform conditions, will give more reliable results than could be obtained in any other way. It is also the belief of the Bureau of Standards that a knowledge as to the nature of our methods of paper testing, as well as the manner in which a paper specification is developed, will tend to convince the trade of the fairness with which this work is carried on.

Royal Institution. — A General Meeting of the Members of the Royal Institution was held on July 7th, Sir James Crichton-Browne, Treasurer and Vice-President, in the Chair. Prof. E. Rutherford was elected a Member. The Chairman announced the decease of Her Grace the Duchess of Northumberland, and the following resolution was passed unanimously:—Resolved, That the Managers and Members of the Royal Institution of Great Britain at the General Meeting this day, desire to record their sincere sympathy and condolence with his Grace the Duke of Northumberland, President of the Royal Institution, and with the House of Percy, on the decease of Her Grace the Duchess of Northumberland.

A GASEOUS SPRING CONTAINING A HIGH PERCENTAGE OF HELIUM.

By E. CZAKÓ and L. LAUTENSCHLÄGER.

Since 1895, when Ramsay (Chemical News, 1895, lxxi., 151) first succeeded in isolating helium, this gas has been found in a large number of minerals, wells, and in gases issuing from the earth's crust. Of those who subsequently took up the subject after Ramsay, Prof. Kayser, of Bonn (Chemical News, 1895, lxxii., 89; *Chem. Ztg.*, 1895, S. 1547), was one of the first to identify helium in natural gaseous springs. By an examination of the hot springs of Wildbad, a resort in the Würtemberg division of the Black Forest, he succeeded in obtaining from 430 cc. of a sample of the gases, which chiefly contained nitrogen, 9 cc. of rare gases containing helium and argon, which corresponds to 2·1 per cent rare gas content.

During some researches which we have lately carried out, and which we have already published along with a detailed description of the apparatus and experiments (Sieveking and Lautenschläger, *Phys. Zeit.*, 1912, xiii., 1043; E. Czakó, *Zeit. Anorg. Chem.*, 1913, Bd. 83), we were able to repeat the investigations on the gases obtained from the hot springs of Wildbad. Commencing with about 1800 cc. of the gases, we obtained, as the mean of several concordant analyses, the following figures (which are corrected for the presence of air):—2·79 per cent carbon dioxide, 94·94 per cent nitrogen, 1·56 per cent argon, and 0·71 helium, thus giving us a value of 2·27 per cent for the rare gas content, a result which agrees satisfactorily with that obtained by Kayser.

Since the researches of Kayser are undoubtedly of real historical importance in the development of the study of the rare gases, we greatly desire to have this short note published in the columns of the Chemical News.

Chemisches Institut, Technische Hochschule,
Karlsruhe (Baden), May, 1913.

THE SCIENTIFIC WEEK.

(*From Our Paris Correspondent*).

Wireless Telegraphy in France and Abroad.

A recent statistic drawn up by the International Bureau of Berne shows that France, the cradle of wireless telegraphy, is at present relegated to the ninth rank as to the number of radiotelegraphic stations opened to the public. It is Canada that possesses the largest number of wireless telegraphic stations open to the general public. Canada has 32 stations. England holds the second place with 25 posts, then comes Russia with 22, Germany 20, Italy 20, Brazil 16, India 11, Spain 2, France 8, Denmark and Norway each 8, Japan 7, &c. But it must be noticed that over and above her 8 public posts, France possesses 11 radiotelegraphic stations for the War Department, the Navy, and the schools. But if France is in a state of evident inferiority as to the number of wireless telegraph stations, her situation is still more precarious if we consider the number of wireless telegraphy posts on vessels and commercial liners. Whereas England has 590 ships supplied with Hertzian posts and Germany 253, France has only 90 vessels that are supplied with radiotelegraphy. The number of radiotelegrams exchanged between the ships and the French posts of wireless telegraphy has increased from 876 in 1908 to 7694 in 1910, to 22,304 in 1911, and 33,786 in 1912. The number of words radiotelegraphed in 1911 reached 238,615, and 371,895 in 1912. It is especially the post of Sainte Marie de la Mer, near Marseilles, that has received and transmitted the greatest number of wireless telegrams. This increase of traffic led the postal administration to consider the advisability of the installation of a new wireless telegraph post at Marseilles.

New Method for Measuring Altitudes.

Explorers often experience great difficulties in determining the altitude of mountains. M. Alphonse Berget, Professor at the Oceanographic Institute, Paris, in a work presented before the Academy of Sciences, has just indicated a simple method which renders it easy to calculate heights by means of the barometer. The employment of a table of logarithms is not necessary; two operations only are sufficient to enable one to measure altitudes rapidly.

The formula employed is simple; the height that is being sought is equal to the relation of the difference of pressure existing between the two places of which one wishes to measure the altitude, and the mean pressure between the two stations, multiplied by the sum of the mean temperature with a constant of 269. This product is multiplied by the coefficient 30. This formula may be thus represented:—

$$Z = 30 \frac{D}{12} (T = 269).$$

By the help of this formula the altitude calculated is equal at about 1/500 m. to the result that would be found by the formula of Laplace.

The Disappearance of the Spots of the Sun.

Quite a whole school of meteorologists wish to connect the atmospherical phenomena with the spots of the sun. It is the spots or the faculæ which, it appears, are the cause of tempests and storms and even of earthquakes. When considerable spots are to be seen on the sun we may infallibly expect most direful catastrophes. Whether they will take place in France, in Europe, in Asia, or America, is not generally stated with any great precision, but if there is an earthquake in Japan, terrible cyclones in the West Indies, and storms and tempests in Europe, according to meteorologists these phenomena are incontestably due to the presence of spots in the sun, with the presence of which they coincide. The same coincidences are remarked for the changes of temperature. If it is hot, it is because a spot is passing on the solar equator. If it is cold, it is because the spots are absent or far removed from the median zone of the sun. If it rains in Paris, why then it is because a large spot has been perceived. But if the weather is fine, the sun is pure and shines without spot or facule. It is thus that everything relating to the weather is explained by the solar spots, but (and the question is one that is at present being discussed) when there are no spots what weather is to be expected?

According to M. Bailland, Director of the Paris Observatory, there have just been seventy days without any solar spot. So, then, ought not atmospherical life to be suspended, so to say, since the primary cause of rain, wind, seismic phenomena, as well as storm phenomena, no longer exists? Logically, then, perpetual fine weather should reign here below; we should now have a general calm, since all atmospheric perturbation of any importance originates from the solar spots, and these spots are absent.

Unfortunately for these theses, or rather these hypotheses, the world has not stopped going round during these seventy days of solar serenity. In France, as all over Europe, and in the whole world, there have been rain, storms, cyclonic and calm periods, and even important seismic shocks, from which especially the inhabitants of Bulgaria have suffered.

Consequently, since these terrestrial phenomena have taken place just the same without solar spots as with them, it becomes logical to conclude that the solar phenomena known by the name of spots or facula have no action whatever of cause and effect upon atmospheric variations; there are only coincidences, the strongest earthquakes, and inversely we may observe tempests and seismic shocks, more or less formidable, although no spots may be visible. That is what has just taken place in this present year 1913, and is what will happen again in some future year of the present century or in the year 2000,

either sooner or later; they are simple coincidences, nothing more.

As to being able to determine from an examination of the sun whether the summer of 1913 will be warm or cold, it would be as easy or not to foretell from the same spots whether on such and such a day it would be fine or not. First of all, it would be necessary to know whether on that day there are to be spots or not; now this prevision is almost impossible. The observers of the sun certainly do good work from a scientific point of view; what can be more beautiful than the study of the Royal day-star of our astronomic system? But when it comes to applying these studies to the forecast of the weather, either at short or long distances of time, why the heliacal science must refrain from pronouncing a judgment. Let solar astronomers be contented with foretelling magnetic fluctuations from the sun's spots; that is already a very fine result, but they had better not venture to foretell the state of the weather. It is an art, as said Lavoisier, that has its principles and its rules, but both are only on the surface of the earth and not in the depths of the heavens, nor in the mysteries of the Infinite.

The Speed of Glaciers.

"The Speed of Glaciers in Winter and the Inanity of the Thermic Theory of their Progression," such is the title of a study that has just been published by M. Vallot, Director of the Mont Blanc Observatory. From the numerous observations made by M. Vallot at the "Sea of Ice" in the massure of Mont Blanc, it appears that no calorific variation either diurnal or annual can penetrate into the interior mass of the glaciers, and that it may be considered as a river that is flowing on in its bed under the simple influence of weight, with a speed that is not sensibly different in winter to what it is in summer.

The Luminosity of Animals.

Many animals possess the power of becoming luminous at will. Glow-worms are the most striking example of this curious phenomenon. Many fish that live in the deep seas possess this same power of becoming luminous.

Scientific men have vainly tried to explain the mechanism of this luminosity. Prof. Armand Gautier has just communicated to the Academy of Sciences a notice of MM. Ville and Denien, of Montpellier, who explain this production of light by the oxidation of a substance secreted by luminous animals, called lophine. This organic azoted substance, under the influence of oxygen, emits a visible luminosity. Potash, in the presence of catalytic elements, such as the ferruginous matters of the blood, likewise provokes the oxidation of the lophine, and consequently forms light. Oxygenated water has also the same property.

In the organisms it is the unstable oxygen of the tissues catalysed by the ferruginous elements of the blood that produces the oxidation of the lophine, and renders animals luminous.

Metallic Beryllium.—Fr. Fichter and Kas. Jablczynski. —Metallic beryllium can be prepared by the electrolysis of a fused mixture of 1 molecule of NaF and 2 molecules of BeF_2. By repeated centrifugation of the impure preparation in a mixture of ethylene bromide and alcohol the comparatively light metal can be separated from the oxide which is present as impurity. The melting-point of beryllium is 1280° ± 20°. The fused metal is very hard, scratches glass, and is only slightly marked by a file. It is steel grey in colour (not silver-white, as Debray has stated). The specific gravity is 1·842 and the atomic volume 4·94. The resistance of beryllium towards water is caused by a layer of oxide formed on the metal. Hot nitric acid, either concentrated or dilute, readily dissolves it. —*Berichte*, xlvi., No. 7.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, June 19th, 1913.

Prof. W. H. Perkin, LL.D., F.R.S., President, in the Chair.

The President announced that, in future, a list of the papers to be read at each Ordinary Scientific Meeting will be advertised in the *Morning Post* on the Wednesday previous to the day of meeting.

Messrs. A. J. Berry and R. Robison were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Alan Milsom Bailey, Lanhill, Chippenham; George Bernard Butler, 10, Malvern Street, Elswick Road, Newcastle-on-Tyne; Alexander Houghton Hay, Essex Wharf, Narrow Street, Limehouse, E.; Harold Frank Tayler, 105, Barrow Road, Streatham, S.W.

A ballot for the election of Fellows was held, and the following were subsequently declared duly elected:— William Love Biggart; Archibald Joseph Brooks; William Rhys-Davies; Jack Cecil Drummond, B.Sc.; Horace Freeman; Roy Gonçalves Glenday, B.A.; James Joseph Hutchinson; Victor Lefebure, B.Sc.; Duncan James Macnaughtan; Ghulam Ali Mahamadi; Marius Maxwell; Ralph Richard Oliver; Percy Bernard Phillips; William Gilbert Saunders; Montagu George Smith; Ebenezer Rees Thomas, M.Sc.; Percy Cyril Lesley Thorne, B.A.; Jeremiah Twomey, M.Sc.; John Stewart Walker; Edwin Longstaff Watson; Ernest John Wilson, M.A.; Thomas Howard Young.

Of the following papers, those marked * were read:—

*189. "*Absorption Spectra and Chemical Reactivity.* Part III. *Trinitrobenzene, Trinitroanisole, and Picric Acid.*" By Edward Charles Cyril Baly and Francis Owen Rice.

The absorption spectra of trinitrobenzene, trinitroanisole, and picric acid were described, and it was shown how the closed force fields surrounding the molecules of these substances are opened up by the use of various basic solvents. In a previous paper (*Trans.*, 1912, ci., 1469) a theory of fluorescence was put forward based on the existence of several stages in the opening up of these closed systems. Whereas previously only one stage had been recognised, three stages have been proved to be produced with the three trinitro-compounds. It was shown how the results explain the formation of the picrates of the hydrocarbons and the nitration of the aromatic compounds.

Discussion.

Referring to the views on the origin of residual affinity advanced by Prof. Baly, and to the remark that previous explanations were "not satisfactory and connected," Dr. Flürscheim said that he was unable to discern any substantial difference between Prof. Baly's views and those he had himself published years before. In support of this he read some passages from one of his papers (*Journ. pr. Chem.*, 1907, [ii.], lxxvi., 185), in which the idea of an equilibrium between the combined and free affinity of an atom was clearly developed. He had repeatedly referred to this publication in subsequent communications to the Society, and based on it some further chemical generalisations, some of which he had already been able to confirm by chemical experiment.

Prof. Baly had merely used different words to express the same meaning. Thus, the term "force lines" used by Baly had already been previously employed by Hugo Kauffmann as a synonym for the term "chemical energy" adhered to by him (Dr. Flürscheim), and it was difficult to imagine chemical energy acting otherwise than in force lines. Similarly, the term "principal and secondary valencies," introduced by Werner and used by Prof. Baly,

was, when applied to the problem of residual affinity, merely a synonym for the term "affinity" used by him (Dr. Flürscheim).

He would therefore be glad to know in what way the views published by Prof. Baly differed from, and represented an advance on, those which he had himself published previously.

*190. "*Derivatives of o-Xylene.* Part V. *5-Bromo-o-4-Xylenol and 6-Bromo-o-4-Xylenol.*" By Arthur William Crossley and Dorothy Jessie Bartlett.

5-Bromo-*o*-4-xylenol, prepared by replacing the amino-group in 5-amino-*o*-4-xylenol by bromine, crystallises in glistening needles, melting at 80°. The *benzoyl* derivative forms transparent plates, melting at 51°, and the *o-nitrobenzoyl* derivative crystallises from ethyl acetate in transparent, rectangular plates, melting at 151—152°.

6-Bromo-o-4-xylenol was prepared from 5-nitro-3-*o*-xylidine by replacing the amino-group by a bromine atom and the nitro-group by hydroxyl. It separates from light petroleum (b. p. 80—100°) in masses of silken needles, melting at 103°. The *benzoyl* derivative crystallises from methyl alcohol in transparent, six-sided plates, melting at 85°, and the *o-nitrobenzoyl* derivative forms glistening needles, melting at 132°.

*191. "*The Presence of Neon in Hydrogen after the Passage of the Electric Discharge through the latter at Low Pressures.*" Part II. By John Norman Collie and Hubert Sutton Patterson.

Since the authors' former communication on this subject (*Trans.*, 1913, ciii., 419), many further experiments have been made. That electrodes are necessary for the production of neon and helium has been disproved; for if a powerful oscillating discharge be passed through a coil of wire wound round a glass bulb containing a little hydrogen, helium with some neon can be detected in the residual hydrogen. It is necessary to free the gas in the bulb as completely as possible from mercury vapour. The experiment was frequently repeated in the same bulb, and even after many weeks' working, helium and neon could still be obtained from the apparatus. The hydrogen and oxygen used in these experiments was repeatedly tested in quantities up to 100 cc., but not a trace of helium or neon was found. The experimental bulb before use was heated to 250° and washed out with oxygen; the oxygen residue did not show the presence of either helium or neon.

Also an apparatus was made where the tube through which the discharge took place was surrounded by a vacuous outer tube. The wires connected to the electrodes in the inner tube passed through the outer tube in glass tubes, so that there could be no discharge from any electrodes in the outer vessel; in this case, also, helium and some neon were found in the outer vessel. The above experiment was made in the following manner. After the tube had been externally heated and pumped until no more gas would come off, a strong current was passed. At once hydrogen began to be evolved from the electrodes; this was pumped off, and an electric spark passed through it to see whether any oxygen was present. A very small contraction occurred; 4·6 cc. remained. This was then gradually put back into the tube, whilst a powerful current was passed through the tube, which was at the same time externally heated with a gas flame. At the end of three hours' sparking, 2·2 cc. of gas remained. This was again put back into the tube and the sparking repeated; at the end of another three hours it had shrunk to about 1·0 cc., and by further treatment it went to 0·4 cc. This hydrogen contained a trace of neon. At this point a crack appeared in the inner tube. From the outer tube only 0·4 cc. had been pumped off; this contained both helium and neon. The inner tube was broken up at once, the two aluminium electrodes were put into a hard glass tube, and fused by a blowpipe in a vacuum; 0·2 cc. of hydrogen was collected. The glass ends of the inner tube were powdered and also heated by means of a blowpipe in a hard glass tube that had been entirely pumped out. Too small an amount of hydrogen to be measured was pumped off. From the above experiment, $4·6 - 1·0 = 3·6$ cc. of hydrogen had apparently disappeared. In the capillary tube between the two ends of the inner tube some black substance had collected where the tube had been very highly heated by the electric discharge. This substance was carbon, for on heating it with a little oxygen it suddenly burnt away with a bright flash, and the oxygen gave a milkiness with baryta solution. Many experiments have also been made with a double tube so constructed that mercury can be run up so as to fill the outer vessel, and drive the gas there up into a small capillary tube with a platinum wire fused through the end of it. The gas can under these conditions be examined by means of an electric discharge from the platinum wire to the mercury. During the whole of an experiment gas is perpetually appearing in the outer tube. It consists largely of hydrogen, together with traces of helium and neon, and of a gas that gives a spectrum of carbon. If it is sparked it rapidly decreases in volume, usually to about one-half and sometimes even less, the carbon spectrum almost entirely disappears, and the hydrogen (and the traces of helium and neon) remain. This same phenomenon also invariably occurs when testing for helium and neon. After the residual hydrogen has been exploded with excess of oxygen, and the residual oxygen has been absorbed by charcoal cooled in liquid air, the gas that remains should be pure helium or neon or a mixture of the two. The spectrum, however, is always a carbon spectrum, and it is only after sparking for some time that the carbon spectrum goes and the pure spectrum of helium and neon takes its place. There is always at the same time a diminution usually of over 50 per cent in the volume of the gas. This gas also is produced in the bulb, round which a wire has been coiled, and through which an oscillating discharge has been passed. It also is produced in a tube containing a piece of platinum foil, placed in the focus of a concave cathode of aluminium, bombarded by cathode stream, so that it becomes red-hot. At first, hydrogen is given, then hydrogen mixed with helium and some neon, then less hydrogen and helium, and some of the gas already mentioned that gives a carbon spectrum. After this apparently no more helium is produced, but an increasingly relatively larger amount of the gas giving the carbon spectrum. If this gas is sparked in contact with mercury vapour, it almost instantaneously disappears, and it has been found impossible to reproduce it, by heating the tube, or varying the pressure in the tube.

As it can be separated from the hydrogen in which it is found by exploding with excess of oxygen and removing that excess by means of charcoal cooled with liquid air, it appears to be a highly uncondensable gas, and not readily oxidised. This result, taken in conjunction with the fact that it gives a carbon spectrum, is very difficult to explain. It is possible that this gas may be the same as that discovered by Sir J. J. Thomson and called by him X_3.

Various experiments have also been made with electrodes other than aluminium. In the case of copper, interesting results were obtained. The hydrogen seemed to disappear more rapidly than when aluminium electrodes were used. Possibly this is due to the fact that a more powerful current can be passed through the tube, and the electrodes therefore heated to a higher temperature. The splashed copper was in parts of a black colour. Even after as much as 5 cc. of hydrogen had been absorbed by a tube, no amount of heating made the gas come off again. The copper splash was dissolved in aqua regia and evaporated to dryness, some water and a little hydrochloric acid added, and the clear solution of the copper salt was then tested with barium chloride. A small, white precipitate was obtained. This has been repeated many times; the copper splash always gives this precipitate. Presumably it is barium sulphate; but it is somewhat difficult to prove the presence of sulphur in the minute amount produced. The actual amount from four different experiments weighed about one-tenth of a milligrm.

Some of it was heated with a little sodium carbonate and carbon, and gave a faint brown stain on silver; also, with hydrochloric acid, a very faint odour of hydrogen sulphide. As ordinary glass contains traces of sulphur, four more experiments were made with lead glass tubes that are quite free from sulphur. Again in every case a precipitate was obtained in acid solution by barium chloride. Three other tubes with respectively magnesium, platinum, and palladium electrodes all gave this precipitate. Every conceivable precaution was taken to test the metals, the reagents, and the electrodes for sulphur, and, except in the case of soda-glass tubes, sulphur was invariably absent.

The results at present arrived at from the experiments given in this note are the following:—

(1) Electrodes apparently are not necessary for the production of the helium and neon.

(2) Hydrogen in considerable quantities can be made to apparently entirely disappear in tubes through which a heavy discharge passes.

(3) A gas is produced in the tubes that gives a carbon spectrum. It entirely disappears when sparked in contact with mercury. It is not readily condensed by charcoal cooled in liquid air, nor easily oxidised by sparking with oxygen.

(4) When copper, platinum, palladium, or magnesium are splashed off in an ordinary vacuum tube containing hydrogen, something is produced that, after dissolving in aqua regia, gives a precipitate in acid solution with barium chloride.

NOTE.—Only one of the authors (J. N. C.) is responsible for the statement that the metallic splashes give, after solution in acids, a precipitate with barium chloride. Since the paper was read he has made further experiments that probably account for its production.

(1) Copper electrodes were used. The solution of the splash in acids was evaporated in *silica* vessels. *No precipitate was obtained.*

(2) The same tube was used again, and the solution of the splash was divided in half. One half (*a*) was evaporated in glass test-tubes, the other half (*b*) was evaporated in silica vessels: (*a*) *gave a precipitate*, (*b*) *gave no precipitate.*

A blank experiment was made with the acids and considerable evaporation in glass test-tubes, and a precipitate was obtained with barium chloride in acid solution.

The hydrochloric acid had been boiled with, and then distilled from, solid barium chloride, and the nitric acid had been treated in the same way with barium nitrate.

There also might be another explanation of the precipitate. The copper electrodes were sealed to the platinum by a little silver solder; some of the silver splashes off; this gives silver chloride, that on evaporation with strong hydrochloric acid dissolves, and is reprecipitated on dilution and addition of barium chloride.

*192. "*The Rotatory Dispersive Power of Organic Compounds.* Part III. *The Measurement of Magnetic Rotatory Dispersion.*" By THOMAS MARTIN LOWRY.

A description was given of apparatus and methods for the measurement of magnetic rotations over a wide range of the visible spectrum.

*193. "*The Rotary Dispersive Power of Organic Compounds.* Part IV. *Magnetic Rotation and Dispersion in some Simple Organic Liquids.*" By THOMAS MARTIN LOWRY.

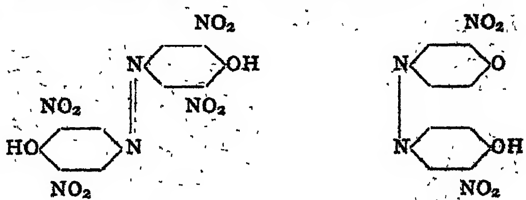
Numerical values were given for the magnetic rotation and dispersion in (1) inactive primary alcohols, (2) active secondary alcohols prepared by Dr. R. H. Pickard, (3) fatty acids, including active valeric acid, (4) ketones, (5) esters and paraffins prepared by Prof. Young, (6) carbon disulphide.

*194. *The Isomerism of* p-*Azophenol.*" BY PHILIP WILFRED ROBERTSON.

p-Azophenol, $HO{\cdot}C_6H_4{\cdot}N:N{\cdot}C_6H_4{\cdot}OH$, as ordinarily prepared, forms yellow crystals containing one molecule of water; there appear, however, to be two yellow modifications, one of which yields, on heating, the anhydrous compound as a dark green, the other as a brick-red variety. Both of these forms have been shown to be stable in dry air under ordinary conditions; at higher temperatures the red is converted into the green, the transition temperature being about 50°. This is possibly not a case of polymorphism, because the difference seems to persist in solution.

In addition to this *a*-azophenol, Willstätter has obtained, by oxidation and subsequent reduction, a β-modification, a red substance incapable of being reconverted into the original compound by physical means. Hantzsch has shown that both substances have exactly the same absorption spectra, and calls this a case of homochromisomerism.

The chemical reactions of the two substances have now been examined. On bromination, they yield different tetrabromo-derivatives, melting at 252° and 271°, and these have also identical absorption spectra. On nitration, *a*-azophenol yields a tetranitro-compound (I.), whilst the β-modification, even with considerable excess of nitric acid, forms only a disubstituted derivative (II.):—



I. II.

It is possible that this difference is due to stereoisomerism, as is indicated in the above formulæ.

DISCUSSION.

Prof. MELDOLA considered that Dr. Robertson had made out a good case in favour of the stereoisomerism of the two forms in the sense of their being the *syn-* and *anti-*modifications. He had no doubt the author had considered the possibility of quinonoid isomerism, since one-half of the molecule admitted of such rearrangement. He asked whether this point had been tested by checking the mobility of the hydroxylic hydrogens by preparing the methyl derivatives, and, if so, whether the two isomerides gave isomeric or identical methyl derivatives.

In reply to Prof. Meldola, Dr. ROBERTSON said that the fact of the two isomerides having the same absorption spectrum precluded the possibility of either possessing a quinonoid constitution. The author differed from Prof. Baly in his contention that an equlibrium mixture in solution might yield two different substances on removal of the solvent, according to whether one started from one or the other isomeride.

*195. "*The Action of Ozone on Cellulose.* Part IV. *Cellulose Peroxide.*" By CHARLES DORÉE.

Ozone acting on purified cotton-cellulose was stated to furnish a peroxide, recognised by its oxidising action on potassium iodide solution (*Trans.*, 1912, ci., 498). Doubts having been cast on the existence of this product, the question has been reinvestigated. In the absence of water, a small amount of peroxide alone is produced, but in air-dry material the quantity of peroxide formed is very much greater, and at the same time the solid insoluble acid and oxycellulose are formed (*loc. cit.*). The amount of "active oxygen" fixed by air dry cotton, mercerised cotton, and lustra-cellulose after eighteen hours' exposure to ozone was 0·0056, 0·0106, and 0·0248 per cent respectively. The peroxide is slowly decomposed on treatment with water, hydrogen peroxide being produced. It is decomposed to the extent of 25 per cent, after heating for two hours at 37°, and almost entirely after two hours at 95°. The activity soon disappears if the material is kept

in the air, but persists for some weeks in a dry atmosphere. The peroxide acts strongly on a photographic plate, sharp negative images of the fibres being obtained in twenty days at 14°, or in six hours at 37°. These properties recall the photographic action of the natural woods described by Russell (*Phil. Trans.*, 1904, cxcvii., 281, &c.), and were shown to be due probably to a similar cause, namely, the gradual production of hydrogen peroxide.

The question of the position in the cellulose complex at which the peroxide oxygen may be attached was discussed, together with the part played by the peroxide in the oxidation of cellulose by ozone.

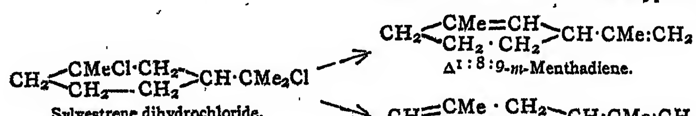
Discussion.

Mr. C. F. Cross believed that the author's paper would be found to explain these observations in terms of a cyclic formula for the unit (C_6) constituent group of the cellulose complex with the "potential" unsaturated position.

He called attention to current articles by H. Gebhardt (especially *Chem. Zeit.*, 1913, xxxvii., 663), discussing the constitution of cellulose from the point of view of its affinities for colouring matters. This author arrived independently at similar conclusions.

*196. "*Sylvestrene. The Constitution of* d-*Sylvestrene and its Derivatives.*" By Walter Norman Haworth, William Henry Perkin, jun., and Otto Wallach.

The authors have been engaged on a detailed investigation of *d*-sylvestrene, prepared from the dihydrochloride by the elimination of hydrogen chloride, and they find that it is mainly a mixture of $\Delta^{1:8:9}$- and $\Delta^{6:8:9}$-*m*-menthadiene.



Sylvestrene dihydrochloride. $\Delta^{1:8:9}$-*m*-Menthadiene. $\Delta^{6:8:9}$-*m*-Menthadiene.

They have also prepared a large number of derivatives of sylvestrene and determined their constitutions.

197. "*The Refractivities of Acenaphthene and its Monohalogen Derivatives.*" By Holland Crompton and Wilhelmina Rebecca Smyth.

The following values have been obtained for the molecular refractions of acenaphthene and its monohalogen derivatives:—

	M_C.	M_D.	M_F.
Acenaphthene	50·84	51·33	52·84
3-Chloroacenaphthene ..	55·53	56·07	57·55
3 Bromoacenaphthene ..	58·97	59·58	61·22
3-Iodoacenaphthene ..	63·42	64·10	66·02

The molecular refraction, M_C, of acenaphthene, calculated from that of naphthalene, is 50·94, and in the case of the halogen derivatives, the values calculated for the molecular refractions from that of acenaphthene agree with the observed. There is therefore nothing abnormal in the behaviour of these compounds.

198. "*The Formation of Cyclic Bases from Aromatic Imides.*" (Preliminary Note.) By Edward Hope and Frederick Russell Lankshear.

The authors have studied the electrolytic reduction of phthalimidine and of N-methylphthalimidine (prepared from phthalimide and N-methylphthalimide respectively), and have succeeded in obtaining excellent yields of dihydro*iso*indole (I.) and N-methyldihydro*iso*indole (II.):—

I. II.

The properties of dihydro*iso*indole thus prepared agree with those given by Gabriel and Pinkus (*Ber.*, 1893, xxvi., 2210) and by Fränkel (*Ber.*, 1900, xxxiii., 2809). As stated by the latter, methyl iodide reacts with dihydro*iso*indole, giving a mixture of the hydriodide and the methiodide.

N-*Methyldihydroisoindole* is a colourless oil with a strong basic odour, and boils at 195—196°/750 mm. It is very soluble in water, and readily distils over in steam, separating in the distillate as a sparingly soluble hydrate, which contains two molecules of water.

The compound also reacts vigorously with methyl iodide, giving a quantitative yield of the methiodide (m. p. 246°). This is identical with the methiodide obtained under similar conditions from dihydro*iso*indole.

This electrolytic reduction process renders simple the preparation of *iso*indole bases, which have hitherto been obtained only by somewhat laborious methods. The authors are engaged in an investigation of these bases, and are carrying out experiments with a view to apply the reduction process to a variety of similar imides.

199. "*The Action of Sulphur Dioxide on Copper at High Temperatures.*" By Clifford Morgan Stubbs.

The depression of the freezing point of copper by dissolved sulphur dioxide has been found to be about 2·54 times that expected if the molecules of the gas remained intact in the solution. This result can be explained on the hypothesis of a partial reaction of the dissolved gas with the molten metal according to the equation $6Cu + SO_2 \rightleftharpoons Cu_2S + 2Cu_2O$.

Complete reaction would give three times the depression calculated from the molecular formula SO_2.

It has been shown that this hypothesis of an equilibrium in the molten metal can be brought into harmony with the solubility results of Sieverts and Krumbhaar. The equilibrium pressures of sulphur dioxide in the univariant system Cu, Cu_2O, Cu_2S (all as solids) have also been measured between 700° and 1050°, the pressure rising in this range of temperature from less than one atmosphere to about seven atmospheres.

200. *The Change of Colour of Metallic Haloid Solutions.*" By Charles Scott Garrett.

Solutions of coloured metallic haloids in general undergo considerable changes of colour on varying the concentration, temperature, or solvent, as well as on the addition of colourless haloid salts. The phenomenon is connected with the presence of varying valency in the parent metal.

It was pointed out that these changes most probably are due to the formation of complex radicles of two types, acidic and metallic radicles, and by quantitative spectrophotometric measurements it has been shown how these two types of complex formation may be distinguished. Copper haloids form acidic complexes, whilst chromium haloids form metallic complexes, but the solvent must be regarded as playing some part in the change.

Bands of selective absorption due to the complexes were found in the case of cupric bromide, cupric chloride, and nickel bromide solutions, by photographing the saturated aqueous solutions in very thin layers.

In the typical cases of copper and chromium haloid solutions it was shown that the various parts of the absorption spectra may be attributed to various entities in the molecules of the salts.

201. "*Hydroxyazo-compounds. The Action of Semicarbazide Hydrochloride on the* p-*Quinones.*" By Isidor Morris Heilbron and James Alexander Russell Henderson.

As indicated in a recent communication (*Proc.*, 1912

xxviii., 256), the condensation products obtained by the action of semicarbazide hydrochloride on the *p*-quinones in equimolecular quantities must, from spectrographic evidence, be regarded as hydroxyazo-derivatives. A further examination of these condensation products has, however, made evident that under certain conditions a few of these hydroxyazo-compounds undoubtedly react tautomerically as semi-carbazones. The authors find further that on salt-formation the hydroxyazo-compounds assume a quinonoid constitution, as is proved by the great similarity of their absorption curves with the typical quinone, tetraphenylquinodimethane. This compound shows a very characteristic band of great persistence in M/10,000 solution, differing in position from the band of *p*-benzoquinone and its homologues, but resembling closely the absorption curves of the nitrophenol salts, and the authors adduce from this that such salts are undoubtedly quinonoid.

A direct relationship has also been found to exist between the molecular weight and position of the absorption band in this series of similarly constituted compounds.

202. "*The Alkaloids of Ipecacuanha.*" (Preliminary Note). By FRANCIS HOWARD CARR and FRANK LEE PYMAN.

In spite of the medicinal importance of ipecacuanha, very little is known about the alkaloids which it contains, although the subject has received a considerable amount of attention. A number of earlier investigations were carried out with a purified amorphous total alkaloid, formerly known as "emetine," but later Paul and Cownley (*Pharm. Journ.*, 1894, [iii.], xxiv., 111) showed that this product contains at least two alkaloids, emetine and cephæline, the latter being a phenolic base, and described methods for their separation and purification. They attributed to emetine the formula $C_{30}H_{44}O_4N_2$ or $C_{15}H_{22}O_4N_2$, and the cephæline, $C_{28}H_{40}O_4N_2$ or $C_{14}H_{20}O_4N_2$, whilst O. Hesse (*Pharm. Journ.*, 1898 [iv.], vii., 98), repeating the work at their request, preferred the formula $C_{30}H_{42}O_4N_2$ for emetine and $C_{28}H_{38}O_4N_2$ for cephæline. Hesse showed that emetine contains four methoxyl groups, whilst the results for cephæline lie between those required for two and three.

The subject has recently been reinvestigated by Keller (*Arch. Pharm.*, 1911, ccxlix., 512), who has brought out the important result that emetine forms a nitrosoamine, and therefore contains an imino-group. He regards it as a secondary tertiary base, containing two methoxyls and at least one hydroxyl group.

In the course of an extended investigation of these alkaloids, the authors have obtained results having an important bearing on the constitution of emetine and cephæline, and think it well to record briefly at the present stage some of their principal conclusions.

A large number of analyses of emetine, and of its hydrochloride, hydrobromide, hydriodide, and nitrate have now been carried out, and these indicate the formula $C_{29}H_{40}O_4N_2$ for this base. This formula is also in better agreement on the whole with the few results obtained by previous investigators than any of the formulæ suggested by them. Cephæline is probably correctly represented by the formula $C_{28}H_{38}O_4N_2$. These formulæ, which are supported by molecular-weight determinations, indicate that each alkaloid contains two nitrogen atoms.

In the stable neutral salts, the bases are combined with two equivalents of acid. Evidence of the existence of basic salts has also been adduced. In each base both nitrogen atoms are present as imino-groups; and these alkaloids are therefore disecondary bases.

Emetine contains four, and cephæline three, methoxyl groups, whilst the latter also contains a phenolic hydroxyl group. All the oxygen atoms contained in them are thus accounted for. Both alkaloids are optically active, the bases being lævorotatory, emetine having $[\alpha]_D -22°$, and cephæline $[\alpha]_D -18°$, whilst the salts are dextrorotatory, anhydrous emetine hydrochloride $[\alpha]_D +16°$ corresponding with $[\alpha]_D +18°$ for the basic ion.

Emetine yields, on oxidation with ferric chloride in aqueous solution, a scarlet, crystalline hydrochloride, which is termed *rubremetine hydrochloride*. Being formed by the removal of eight hydrogen atoms from emetine, it has the formula $C_{29}H_{32}O_4N_2,HCl,6H_2O$. It melts at 127—128° (corr.), contains four methoxyl groups, and is monobasic. When emetine is oxidised with a large amount of potassium permanganate in aqueous acetone solution, 6:7-dimethoxy*iso*quinoline-1-carboxylic acid is formed, identical with the substance previously obtained by Goldschmidt by the oxidation of papaverine; *m* hemipinic acid has also been observed amongst the oxidation products.

Cephæline, on oxidation, behaves differently from emetine, ferric chloride giving rise to two crystalline oxidation products:—(i.) a *hydrochloride*, $C_{24}H_{24}O_7N_2,HCl,5H_2O$, melting at 249—250° (corr.), and containing three methoxyl groups but no hydroxyl group, (ii.) a *hydrochloride*, $C_{17}H_{21}O_6N,HCl,4H_2O$, melting and decomposing at 158° (corr.), after drying at 100°, and containing two methoxyl groups and a hydroxyl group.

A crystalline N-methyl derivative of cephæline, melting at 194° (corr.), has also been obtained.

The results are being elaborated and extended, and it is hoped to communicate them fully to the Society later in the year.

203. "*Dibenzoyldiaminoacetic Acid.*" By PAUL HAAS.

When α-hydroxyhippuric acid—

$$C_6H_5 \cdot CO \cdot NH \cdot CH(OH) \cdot CO_2H,$$

is heated to 150°, it is converted into dibenzoyldiaminoacetic acid, $(C_6H_5 \cdot CO \cdot NH)_2CH \cdot CO_2H$, in a 40 per cent yield; the latter substance, on hydrolysis, decomposes into benzamide and glyoxylic acid.

204. "*The So-called Calcium β-Diglycerylphosphate.*" (A Correction.) By FRANK TUTIN.

In a paper published by the present author and Mr. Hann (*Trans.*, 1906, lxxxix., 1754), a calcium salt, melting at 249—250°, was described, which, on hydrolysis with dilute acids, gave a small yield of β-glycerylphosphoric acid. Analyses of the calcium salt mentioned gave results in harmony with the conclusion that it had the composition $C_{12}H_{28}O_{16}P_2Ca$, provided it were assumed that thirteen molecules of water of crystallisation were also present. It was therefore regarded as hydrated calcium β-diglycerylphosphate.

It has now been ascertained that this conclusion cannot be correct, since the calcium salt in question contains chlorine (about 38 per cent on the air-dried material). This fact, however, does not affect the identity of the β-glycerylphosphoric acid prepared by the hydrolysis of the calcium salt, the formation of which was one of the objects of the above-mentioned investigation.

205. "*Some Derivatives of Desylamine.*" By ALEX. MCKENZIE and FRED BARROW.

The authors have studied the conversion of phenylaminoacetic acid into desylamine, with the primary object of aiding an investigation, which is at present in progress, on the isolation of the optically active modifications of the base.

α-Phthalyliminophenylacetyl chloride, when acted on by benzene and aluminium chloride, gave desylphthalimide (compare Pfaehler, *Ber.*, 1913, xlvi., 1700), from which desylamine can be obtained.

A mixture of desylphthalimide and dibenzoylstilbene was produced by the interaction of desyl chloride and potassium phthalimide in presence of nitrobenzene at 150—160°.

2:4:5-Triphenyloxazole was prepared by the dehydration of benzodesylamide and concentrated sulphuric acid.

The action of various Grignard reagents on desylamine hydrochloride has also been investigated.

(To be continued).

NOTICES OF BOOKS.

Iron and Steel. By O. F. Hudson, M.Sc., A.R.C.S., with a Section on Corrosion by Guy D. Bengough, M.A., D.Sc. London: Constable and Co., Ltd. 1913.

The aim of this book—to put before students and practical men the elementary principles of the metallurgy of iron and steel—is well fulfilled, and it can be recommended as a good introductory text-book, describing the outlines of foundry practice, the properties of irons and steels, and the constitution of the iron-carbon alloys. The photo micrographs of the latter are well reproduced, and a clear explanation is given of the construction and interpretation of equilibrium diagrams. Dr. G. D. Bengough has contributed to the book a chapter on the corrosion of iron and steel, in which a full review is given of modern work and theories on the subject.

The Function and Scope of the Chemist in a Pharmaceutical Works. By Charles Alexander Hill. London: The Institute of Chemistry of Great Britain and Ireland. 1913.

This lecture, which was delivered before the Institute in March, 1913, discusses some aspects of the work of a chemist in pharmaceutical works. The manufacture of pharmaceutical chemicals and preparations is treated in outline, and some account is given of the different processes involved. The control of raw materials, finished products, &c., is discussed shortly, and the effect of the analytical control of commercial products is made the subject of some practical remarks. The investigation or research work which may fall to the lot of a works chemist is considered, and the part he can play on the commercial or less technical side is also pointed out. The lecturer aimed at stimulating the activity of the works' chemist, and showing by actual examples how the man who has had a laboratory training but no experience in a factory may apply his knowledge to the best advantage of himself and his employer.

The Qualitative Analysis of Medicinal Preparations. By H. C. Fuller, B.S. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1912.

The task of determining the constituents of a mixed medicine is one which is exceedingly tedious and complicated, and ordinary text-books of analysis are of very little use, since they take no account of the possible mutual action upon one or another of the different drugs which may be present, while the numerous articles on the subject which have appeared in periodical literature are widely scattered and difficult of access. The author of this book has worked out a systematic scheme by which a medicinal preparation can usually be completely analysed, the ingredients being first separated into large groups, then into smaller groups, and finally identified as individuals. Some of the tests are new, while others have been brought together from various sources, and the scheme is really comprehensive, including all the usual medicinal substances.

Dairy Technology. By C. Larsen, M.S.A., and Wm. White, B.S. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1913.

This book treats of the technology of the dairy, the preparation of dried and condensed milk, renovated butter, and various other dairy products. Analytical methods and the more purely scientific side of the subject are not treated in it, and throughout American methods and practice are chiefly discussed. But inspectors, dairy owners, and the marketers of dairy produce in this country can learn something from it. Copious statistics of city milk supplies are given, and plans for the improvement of the conditions under which milk, &c., is sold are suggested. The pasteurisation of milk is discussed, and the advantages and disadvantages of the process are compared at length, while methods of standardisation of milk and cream are also described, with plenty of numerical examples. The making of ice-cream both on the small and large scales is fully treated, and chapters are added on the important and growing industries of the manufacture of milk sugar, casein, milk powders, and the preparation of fermented milks.

Service Chemistry. By Vivian B. Lewes, F.I.C., F.C.S., and J. S. S. Brame, F.C.S. Fourth Edition. London: Edward Arnold. 1913.

The importance of a knowledge of chemistry and metallurgy to naval and military officers is nowadays fully recognised, and the earlier editions of this book met with a well-deserved success which will undoubtedly be shared by the latest issue. The authors have kept the balance very well between the purely scientific side of the subject and the technical applications, and the discussion of every practical problem is led up to by a thorough explanation of the principles involved. The nature and causes of explosions and modern explosives are fully treated, and fuel problems, the corrosion of metals, the properties of alloys, boiler incrustations, and kindred subjects are discussed with special reference to the knowledge of them which the naval or military officer should possess.

The Journal of the Alchemical Society. Edited by H. Stanley Redgrove, B.Sc. (Lond.), F.C.S. Vol. I. Part 3. London: H. K. Lewis. 1913.

The Alchemical Society was founded in 1912 for the study of the works and theories of the alchemists, and some interesting papers have been read before its meetings and subsequently published in the *Journal*. An ably written paper by Mr. Sijil Abdul-Ali on "An Interpretation of Alchemy in Relation to Modern Scientific Thought" is contained in No. 3 of the *Journal*, together with an abstract of the discussion which followed the reading of it before the Society.

Blue Book of Safety Appliances. London and Glasgow Messrs. Wallach Bros., Ltd.

This booklet contains fully illustrated particulars of the patent oxygen apparatus designed by Messrs. Wallach Bros., Ltd., as well as many different kinds of helmets, masks, and other safety appliances, first aid cabinets, &c. A copy of the memorandum by H.M. Chief Inspector of Factories as to the use of water gas and other gases in factories and a very favourable report by Mr. B. H. Thwaite, C.E., on the various appliances are reproduced.

Die Fabrikation der Tonerde. ("The Manufacture of Clay"). By Dr. phil. A. Berge. Halle-a.-S.: Wilhelm Knapp. 1913. (M. 3.80).

The great advances which have been made in recent years in methods of manufacturing clay are well described in this monograph, which is designed to meet the want which has for some time been felt for a concise handbook on the subject, which, while not entering into full details, gives a clear and adequate summary of modern developments of the industry. The preparation of clay from bauxite is naturally given special prominence, and the treatment of the raw material, the ignition process, extraction of melt, &c., are carefully described. A short account is given of the uses of clay, including fused clay and artificial gems, and the preparation of aluminium metal is very briefly treated.

CORRESPONDENCE.

HUMPHREY OWEN JONES MEMORIAL FUND.

To the Editor of the Chemical News.

SIR,—The Committee formed to carry out the generally expressed desire that some suitable memorial of the late Humphrey Owen Jones, F.R.S., should be established, has received subscriptions amounting to about £3600. It is proposed to devote the sum collected to the endowment of a teaching post in Physical Chemistry in the University of Cambridge.

The Committee desires to close the subscription list at the end of this month, and requests further intending subscribers to send their contributions to the account of the H. O. Jones Memorial Fund, Messrs. Barclay and Co.'s Bank, Cambridge, before that date.—I am, &c.,

WILLIAM J. POPE,
Chairman of the Committee.

The Chemical Laboratory, Cambridge,
July 7, 1913.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clvi., No. 16, April 21, 1913.

Tetra-alkylation of Cyclohexanone and β-Methylcyclohexanone, and Tri-alkylation of Menthone.—A. Haller.—By the help of sodamide it is possible to replace all the atoms of hydrogen united to the two atoms of carbon attached to the CO group in a cyclohexanone (whether substituted or not) by hydrocarbon radicles. In the cases of the simple cyclic ketone and its β-methyl derivative condensation products are always formed, the latter condensing less easily than its lower homologue, while menthone gives no condensation products. With cyclohexanone itself this condensation becomes more marked when attempts are made to introduce homologous radicles superior to methyl, so that only very few substituted derivatives are obtained. The tetra-, penta-, and hexa-alkylcyclohexanones do not combine with either hydroxylamine or semicarbazide, and in ether, benzine, and toluene they resist the action of sodamide. In xylene they are split up, yielding very complex basic derivatives.

Thermic Study of Uranyl Nitrate and its Hydrates.—M. de Forcrand.—From the heat of solution of the hydrates of uranyl their boiling-points can be calculated. The hexahydrate appears to be a compound, the efflorescence tension of which is not negligible at the ordinary temperature and the crystals may contain a little less than $6H_2O$. The trihydrate is more stable, but the efflorescence tension is not quite negligible at the ordinary temperature. The dihydrate is still more stable, but at 98° it very slowly loses one of its molecules of water, while at 110° the other molecule is driven off after 150 hours.

Dissociation of Gaseous Compounds by Light.—Daniel Berthelot and Henry Gaudechon.—The law according to which in a given family of elements the stability of the compounds towards light decreases as the atomic weight increases is verified in the nitrogen and carbon families, as shown by the study of ammonia, phosphoretted hydrogen and arseniuretted hydrogen, and of methane and hydrogen silicide.

No. 17, April 28, 1913.

Methylation of Isovalerone by Sodamide and Methyl Iodide.—A. Haller and Edouard Bauer.—When sodamide and methyl iodide act on isovalerone the successive products are symmetrical dimethylisovalerone, trimethylisovalerone, and symmetrical tetramethylisovalerone. The last ketone yields neither oxime nor semicarbazone. When reduced with sodium and absolute alcohol it gives the corresponding alcohol.

Absorption of Neon by Electrodes of Luminescent Tubes.—Georges Claude.—If a luminescent tube is filled with neon containing 1 per cent of helium the latter is rapidly absorbed, and is found in an increased proportion in the gases disengaged from the volatilised metal. A small amount of neon present in an atmosphere of helium is not similarly eliminated. Nitrogen resembles helium in being much more readily absorbed than neon, and apparently the resistance of neon to absorption by electrodes is a true characteristic of this substance, which is also remarkable for its power of causing the cathodic volatilisation of certain metals and for its very feeble dielectric cohesion.

Density of Double Salts.—Ed. Chauvenet and G. Urbain.—From experiments performed with the double chlorides of copper and ammonium it appears that the following law may hold good in certain cases:—The molecular volume of a double salt is frequently equal to the sum of the molecular volumes of its constituents. Thus the molecular volume behaves like the other properties (colour, magnetism, chemical properties, &c.), with reference to which the salt in question appears to be a perfect double salt.

Quantitative Study of the Absorption of Ultraviolet Rays by Ketones, Diketones, and Ketonic Acids.—Jean Bielecki and Victor Henri.—All substances of formula $C_nH_{2n+1}COC_pH_{2p+1}$ possess an absorption band between 2700 and 2800, its position and height depending upon the values of n and p. The linking of the carbon atoms in the monoketones and the position of the ketonic group in the chain influence the absorption. When two ketonic groups are present in the same molecule an exaltation of the absorption band is observed, but the position of the maximum is not affected. If ketonic and carboxyllic groups are both present the absorption characteristic of the carboxyl group is raised and that of the carbonyl group is lowered. When a substance can exist in both the ketonic and enolic forms the absorption varies with the proportion of the two forms present.

Action of Formic Acid on Triphenylmethane Dyes.—A. Guyot and A. Kovache.—When formic acid acts on triphenylmethane dyes normal reduction first takes place, but the leucobase formed is ultimately reduced and split up. There is evidently a complete continuity between the dyes and the carbinols deprived of all auxochrome, and the only difference between the two groups of compounds lies in their reactive power, which depends upon the basicity of the molecules.

No. 19, May 31, 1913.

Preparation of Dicyclohexylbutanes.—Paul Sabatier and M. Murat.—Theoretically there should be nine isomeric dicyclohexylbutanes, six derived from normal and three from isobutane. None of these have been known before, but the authors have now prepared five of them (three from normal butane) by the direct hydrogenation of the corresponding hydrocarbons in presence of nickel. Thus from symmetrical diphenylbutane 1.4-dicyclohexylbutane is obtained, and from 1.2-diphenylbutane 1.2-dicyclohexylbutane.

Degradation of Mono and Dibasic Saturated Acids.—Th. Barbier and R. Locquin.—Lower homologues can be obtained from the saturated acids by first transforming the carboxyl into a tertiary alcohol group by the action of two molecules of CH_3MgI on the ethyl or methyl ether:—

$$R.CH_2.CO.OCH_3 + 2CH_3MgI \rightarrow R-CH_2-C(OH)<^{CH_3}_{CH_3}.$$

Then the tertiary alcohols or the unsaturated hydrocarbons derived from them by dehydration are oxidised:—

$$RCH_2COH<^{CH_3}_{CH_3} + O_3 = R.COOH + CH_3.CO.CH_3 + H_2O.$$

The ketones can be used for this transformation instead of the ether salts. If the COOH group is attached to a CH_2 the group $\begin{matrix}CH_3\\CH_3\end{matrix}>OH$ is eliminated as $CH_3.CO.CH_3$, while the neighbouring CH_2 is transformed into COOH. This the initial acid is converted into its next lower homologue. When the COOH is attached to a substituted carbon atom the principal product of oxidation is a ketone. The dibasic acids behave like the monobasic acids, both carboxyl groups being attacked.

Solid Phosphides of Hydrogen.—Louis Hackspill.—When the alkaline phosphides of formula P_5M_2 are treated with hydrochloric acid or acetic acid (very dilute), a yellow phosphoretted hydrogen of formula P_5H_2 is obtained. The existence of P_2H or $P_{12}H_6$ seems doubtful. The author, in collaboration with M. R. Bossuet, has obtained a series of metallic phosphides corresponding to the acid P_5H_2.

Phenyl-α-oxycrotonic Acid.—J. Bougault.—Good yields of phenyl-α-oxycrotonic acid can be obtained by saponifying the amide with oxalic acid. In the course of his researches on the preparation of phenyl-α-oxycrotonic acid the author has obtained an acid of formula $C_{10}H_{10}O_3$, which results from a new isomerisation of the original acid. It appears to be $C_6H.COH=CH.CH_2.CO_2H$, and is thus the enol form of benzoylpropionic acid into which it is transformed by caustic alkalis and strong acids. It is a crystalline substance fusing at 91°.

1-Benzoyl-2-Phenyl-Δ_2-Cyclopentene.—Edouard Bauer.—Sodamide brings about the condensation and cyclisation of dibenzoylbutane, giving 1-benzoyl-2-phenyl-Δ_1 cyclopentene fusing at 53°, and its Δ_2 isomer fusing at 98°. The latter gives with sodamide a derivative which reacts with alcoholic iodides with formation of an alkyl ketone, which reacts with sodamide like a trialkylacetophenone. In this reaction the carbon chain is broken at the CO group, with formation of 1-methyl-2-phenyl-Δ_2-cyclopentene and benzoic amide or of benzene and the amide of 1-methyl-2-phenyl-Δ_2-cyclopentene-1-carboxylic acid.

Bulletin de la Société Chimique de France.
Vol. xiii.-xiv., No. 9, 1913.

Uranyl Formate.—Gaston Courtois.—When a concentrated aqueous solution of uranic acid crystallises with formic acid only one hydrate is formed at the ordinary temperature, the neutral formate, $(HCO_2)_2UO_2.H_2O$. When dried over sulphuric acid this hydrate is very stable up to 100°; when the temperature is raised it gives up water up to 150° and then very slowly decomposes. In concentrated aqueous solution the salt decomposes with formation of a basic crystallised salt of formula $(HCO_2)_2UO_2.H_2O.NO_3.3H_2O$. This basic salt is decomposed by prolonged boiling, giving finally uranic acid, UO_3H_2O. The properties of the author's salt are very different from those attributed by Oechsner de Coninck and Raynaud to uranyl formate.

Zirconium Carbonates.—Ed. Chauvenet.—Zirconium oxide combines with carbonic acid to give hydrated orthocarbonates, neutral and basic. When these compounds are heated they are converted into more and more basic and hydrated derivatives, but no anhydrous carbonate is obtained, and apparently no anhydrous carbonate, either neutral or basic, can exist.

Benzoyl Cyanhydrines, Benzoyl-amides of Aldehydes, and the Corresponding Acid Alcohols. M. Aloy and Ch. Rabaut.—The cyanhydrines of formic, propyl, and isobutyl aldehydes can be prepared by allowing a molecule of benzoyl chloride to act on an equimolecular mixture of the aldehyde and potassium cyanide in aqueous solution. In contact with concentrated HCl the cyanhydrines readily yield the corresponding amides from which he acids are obtained by saponification. The benzoyl yanhydrine of furfurol can be obtained similarly, but it does not give an amide or acid.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xlvi., No. 7.

Behaviour of Hydrogen towards Palladium.—A. Gutbier, H. Gebhardt, aud Berta Oltenstein.—In agreement with the results of Paal and Amberger the authors have found that as the temperature is lowered there is a very considerable increase in the amount of hydrogen occluded by palladium. At +20° the minimum occlusion occurs. The preparations of hydrogen-palladium obtained are pyrophoric.

Action of Alkali Arsenite on Ethyl-disulphide.—A. Gutmann.—Ethyl disulphide acts on tertiary sodium arsenite in the cold, giving sodium arsenate and ethyl mercaptan. This oxidising action is remarkable, since the disulphide contains no oxygen, but it is evidently due to the peroxide character of the disulphide; it acts upon water, removing hydrogen and liberating oxygen :—

$$\begin{matrix}C_2H_5S\\C_2H_5S\end{matrix}+H_2O=2C_2H_5.SH+O,$$

and the oxygen then converts the arsenite into arsenate.

Stable Chromous Oxide Compounds.—Wilhelm Traube and W. Passarge.—Certain chromous oxide salts form with free hydrazine stable salts which still contain divalent chromium, but unlike other chromous salts are quite stable in air. They can be exposed to atmospheric oxygen for a day without undergoing any change, and some of them are not even oxidised when suspended in water. If, however, they are dissolved in acids or in ammonia they readily absorb oxygen from the air. The following chromous hydrazine salts have been prepared :—$CrCl_2.2N_2H_4$, $CrBr_2.2N_2H_4$, $CrI_2.2N_2H_4$, and $CrSO_4.(N_2H_4)_2.H_2SO_4$.

Anhydrous Chlorides of Iridium of Four Different Valencies.—Lothar Wöhler and S. Streicher.—The formation of anhydrous $IrCl_4$ occurs very slowly below 100° from trichloride and chlorine under high pressure. The complex H_2IrCl_6 loses HCl above 100°, yielding chlorine with a higher pressure than 1 atmosphere. The trichloride can very easily be prepared from the metal and chlorine at 600°. In chlorine, at a pressure of 1 atmosphere, the trichloride can exist at temperatures ranging from 763° to 100°. The chlorination of the metal and the dissociation of the trichloride in certain conditions may lead to the formation of a dichloride or a monochloride. The former is capable of existence only between 763° and 773°, and the latter between 773° and 798° in an atmosphere of chlorine.

Atti della Reale Accademia dei Lincei.
Vol. xxii. [i.], No. 5, 1913.

Notes on the Constitution of the Azoxy Compounds.—Angelo Angeli.—When an azo compound, $C_6H_5N=N.C_6H_5$, is treated with bromine or nitric acid the bromine atom or nitric radical takes up the para position in the $N.C_6H_5$ residue, probably with the intermediate formation of a dibromide :—

$$=N.C_6H_5+Br_2 \longrightarrow \begin{matrix}=N.C_6H_5\\ |\\ Br_2\end{matrix} \longrightarrow =N.C_6H_4Br+HBr.$$

Ordinary azoxybenzene gives a dibromide which readily loses HBr, forming a parabromo derivative. Thus α-parabromoazoxy benzene is probably $\begin{matrix}C_6H_5.N=N.C_6H_5,\\ \|\\ O\end{matrix}$ and the β-compound is $\begin{matrix}C_6H_5.N=N.C_6H_5\\ \|\\ O\end{matrix}$. The α-derivative with bromine gives a dibromo derivative identical with that obtained by the action of hydrogen peroxide on paradibromoazobenzene. Apparently the atom of oxygen protects the aromatic residue united to the same nitrogen atom from the action of the substituent.

THE CHEMICAL NEWS

VOL. CVIII., No. 2799.

SOLUBILITIES OF THE RARE EARTH SALTS OF BROMO-NITRO-BENZENE-SULPHONIC ACID (1 : 4 : 2).*

By S. H. KATZ and C. JAMES.

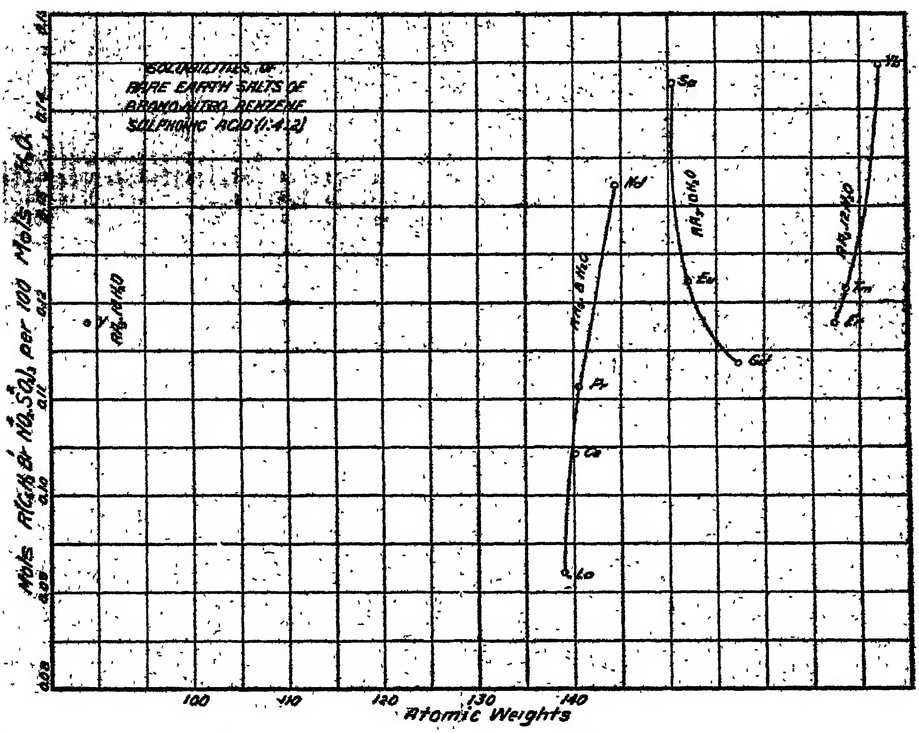
HOLMBERG (*Chem. Centr.*, 1906, ii., 1595) used meta-nitro-benzene sulphonic acid very successfully for the separation and purification of neodymium. Derivatives of this acid therefore gave promise of being useful in work on the rare earths.

Bromo-nitro-benzene sulphonic acid (1 : 2 : 4) was prepared by the method of Limprecht (*Ber.*, viii., 456). The lanthanum, cerium, and yttrium salts of this acid were prepared and found to be very soluble. By spontaneous evaporation yellow warty crusts finally formed, which were useless for crystallising.

Bromo-nitro-benzene-sulphonic acid (1 : 4 : 2) was prepared by the method of Augustin and Post (*Ber.*, viii., 1559). In sulphonating the bromo-nitro-benzene it was treated with two and one-half times its weight of sulphuric acid containing 40 per cent free SO_3 at 100°, until the mixture dissolved completely in water, which required about twenty-four hours. The product was treated with $BaCO_3$ and excess of soluble barium then removed by treating with the proper amount of H_2SO_4. Considerable other acid material besides the bromo-nitro-benzene-sulphonic acid (1 : 4 : 2) was formed. The latter crystallised well from a boiling, saturated, aqueous solution. A pure material was obtained by a series of fractional crystallisations of the crude acids. The yield was about 30 per cent. Salts of lanthanum, cerium, yttrium, and ytterbium were prepared. All crystallised nicely from solution, forming salts only very faintly tinged with the yellow colour of the acid. The properties were such that this acid was seen to offer opportunity for a definite comparative study of the properties and solubilities of a series of rare earth salts.

The compounds of the acid with yttrium, lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, erbium, thulium, and ytterbium were prepared and crystallised from solution. The first crop of crystals only were used in this work.

Composition was found by determination of water of crystallisation by heating the air dry crystals to 200°, and by determination of R_2O_3 by means of the oxalate precipitation and ignition. In the case of praseodymium the oxalate was titrated with a standard $KMnO_4$ solution. The results are given in Table I.



In the case of the erbium, thulium, and ytterbium compounds, which contained twelve molecules of water of crystallisation, the water could not be determined, because at the temperature used for the other salts these were charred, while at a lower temperature the water was not all evolved.

The colours of the salts of praseodymium, neodymium, samarium, erbium, and thulium were not modified noticeably by the colour of the acid radical. The compounds containing eight molecules of water of crystallisation formed needle-like crystals; those containing ten molecules, thin orthorhombic plates, and those containing twelve molecules less regular plates and needles.

The solubilities were determined after allowing equilibrium to become adjusted by rotation in a thermostat

* Contribution from the Chemical Laboratory of New Hampshire College.

TABLE I.

1 4 2	H_2O (per cent). Cal.	Found.	R_2O_3 (per cent). Cal.	Found.
Y $(C_6H_3Br.NO_2.SO_3)_3.10H_2O$	16·29	15·90 15·98	10·16	10·13 10·07
La $(C_6H_3Br.NO_2.SO_3)_3.8H_2O$	12·80	12·80 12·90	14·46	14·41 14·38
Ce $(C_6H_3Br.NO_2.SO_3)_3.8H_2O$	12·78	12·60 12·60	14·58	14·50 14·58
Pr $(C_6H_3Br.NO_2.SO_3)_3.8H_2O$	12·78	13·05 12·78	14·59	14·40 14·43
Nd $(C_6H_3Br.NO_2.SO_3)_3.8H_2O$	12·74	12·82 12·66	14·88	14·79 14·82
Sa $(C_6H_3Br.NO_2.SO_3)_3.10H_2O$	15·35	15·01 14·96	14·86	14·90 14·90
Eu $(C_6H_3Br.NO_2.SO_3)_3.10H_2O$	15·34	14·98 15·33	14·91	14·83 14·98
Gd $(C_6H_3Br.NO_2.SO_3)_3.10H_2O$	15·27	14·93 14·99	15·36	15·43 15·47
Er $(C_6H_3Br.NO_2.SO_3)_3.12H_2O$	—	—	15·60	15·62 15·62
Tm $(C_6H_3Br.NO_2.SO_3)_3.12H_2O$	—	—	15·68	15·64 15·43
Yb $(C_6H_3Br.NO_2.SO_3)_3.12H_2O$	—	—	15·96	15·95 16·02

TABLE II.

1 4 2	Mols. anhydrous salt per 100 mols. H_2O.	Per cent anhydrous salt.
Y $(C_6H_3Br.NO_2.SO_3)_3$	0·1178	5·739
La $(C_6H_3Br.NO_2.SO_3)_3$	0·09207	4·771
Ce $(C_6H_3Br.NO_2.SO_3)_3$	0·1043	5·559
Pr $(C_6H_3Br.NO_2.SO_3)_3$	0·1112	5·730
Nd $(C_6H_3Br.NO_2.SO_3)_3$	0·1322	6·762
Sa $(C_6H_3Br.NO_2.SO_3)_3$	0·1427	7·272
Eu $(C_6H_3Br.NO_2.SO_3)_3$	0·1222	6·310
Gd $(C_6H_3Br.NO_2.SO_3)_3$	0·1137	5·938
Er $(C_6H_3Br.NO_2.SO_3)_3$	0·1178	6·056
Tm $(C_6H_3Br.NO_2.SO_3)_3$	0·1214	6·379
Yb $(C_6H_3Br.NO_2.SO_3)_3$	0·1397	7·294

kept constant at 25°. The results in Table II. are averages of duplicates.

The solubilities plotted against atomic weights are shown graphically in the accompanying diagram. It is seen that, with change in the water of hydration, there is a change in direction of the solubility curve, which amounts to a reversal of the slope. The phenomenon shown may be compared to that producing the change in the general direction of the temperature-solubility curve of a single salt forming various molecular compounds with water at different temperatures. That is, with a break in the general direction of the solubility curve there is a change in the nature of the compound.

Work on the separation of various rare earths by crystallising salts of bromo-nitro-benzene sulphonic acid (1 : 4 : 2) is now under way in this laboratory.

Durham, N.H.

Two Characteristic Colour Reactions of Phenylalanine.—L. Chelle.—To identify phenylalanine a little of the substance is dissolved in 4 cc. of H_2SO_4 in the cold and the solution is divided into two portions. One drop of formol is added to the one, when an orange colouration, rapidly turning brown, is produced. One drop of an alcoholic solution of paraldehyde is added to the other, and after ten minutes a lemon colouration is produced. After an hour it exhibits a green fluorescence. By these two reactions one milligrm. of phenylalanine can be detected. The second test is most useful for quantitative determination, which can be performed by comparing the colourations obtained after one hour.—*Bulletin des Travaux de la Société de Pharmacie de Bordeaux*, vol. liii., March, 1913.

THE ABSORPTION OF LIGHT BY WATER CHANGED BY THE PRESENCE OF STRONGLY HYDRATED SALTS, AS SHOWN BY THE RADIOMICROMETER.*

NEW EVIDENCE FOR THE SOLVATE THEORY OF SOLUTION.

By J. SAM GUY, E. J. SHAEFFER, and HARRY C. JONES

THE use of the radiomicrometer in studying the absorption spectra of certain substances has already been discussed by Jones and Guy (*Phys. Zeit.*, 1912, xiii., 649). The radiomicrometer was used in the study of absorption spectra of solutions, rather than the grating spectrograph and the photographic plate, because the radiomicrometer enabled us to measure not only the positions of the different lines and bands, but also to study quantitatively their intensity. Further, the radiomicrometer, as has already been pointed out, enables us to study the absorption spectra of solutions over a much greater range of wave-lengths than the photographic method.

In building a radiomicrometer that would be adapted to this work, that is, with sufficient sensibility and with a short period, one of the greatest difficulties encountered was to obtain copper wire free from iron. This was a necessity, since the presence of an appreciable quantity of iron in the copper gave rise to a "magnetic control" which rendered the instrument unstable and the zero point inconstant. This difficulty was for the most part overcome, due to the kindness of Messrs. Leeds and Northrup, of Philadelphia, and of R. W. Paul, of London. They both furnished us with copper wire so free from iron that the "magnetic control" could easily be regulated. By means of this wire and the thermoelectric junction already described (*Phys. Zeit.*, 1912, xiii., 651), a most sensitive radiomicrometer which at the same time had a very short period was built. Work with salts of neodymium and praseodymium, the results of which were recorded in the *Physikalische Zeitschrift*, was done with this instrument.

At the beginning of the present academic year the absorption spectra of solutions of a large number of salts of different metals were mapped out. The spectra of these salts were compared with the absorption of water, using the same depths of water as the water in the various solutions. It was soon found that the absorption of the solution was *less*, and in some cases *very much less*, than that of the layer of water having a depth equal to the depth of the water in the solution. The depth of water in the solution was determined from the concentration of the solution and from its specific gravity.

It is obvious that the above is a very remarkable fact. The dissolved substance could not have less than no absorption of light, the assumption having been made, up to this time, that in an aqueous solution the water present absorbs just as much as pure uncombined water. The above result is directly at variance with everything that was known at the time.

It became at once obvious that we could not measure the absorption spectrum of a solution, subtract from it the absorption due to water, and conclude that the remainder was the absorption due to the dissolved substance, since the water in the solution has very different absorption from an equal amount of pure uncombined water.

We then carried out a number of experiments in cells whose depths could be easily and accurately adjusted, with different substances, in the following manner:—We measured the absorption spectra of a number of different substances. We then measured the absorption spectra of water having the same depths of layer as the water in the solutions. We found that for certain substances the pure water was more opaque than the solutions, and for other substances the water was more transparent. The percentage transmission, that is, the deflection of the radio-

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* This investigation was carried out with the aid of a Grant generously awarded by the Carnegie Institution of Washington to H. C. Jones. From the *American Chemical Journal*, xlix., No. 4.

micrometer for the solution, divided by the deflection for water, for the first named substances amounted to more than 100 per cent. Pure water had a different absorption from an equal depth of water in the solution, and since this difference varied from one dissolved substance to another, it is obvious that this method was not the one to be followed. It would be very difficult, not to say impossible, to interpret the results obtained by dividing the radiomicrometer deflection for the solution by those for pure water. We should simply be obtaining the transmission of the solution in terms of pure water, which was not what was desired.

What we want to know is the actual absorption or transmission of the solution, and then that of pure water having a depth of layer that was just equal to that of the water in the solution. These two sets of results could then be compared with one another.

In this earlier work we had, however, noted that solutions of those substances which are largely hydrated are more transparent than pure water having the depths of the water in the solutions in question. Solutions of non-hydrated substances, or of only slightly hydrated substances, provided the substances themselves do not absorb light, are not more transparent than pure water having the same depths as the water in the solution.

It would seem from this observation that water combined with the dissolved substance had less absorption of light than pure uncombined water. To test this quantitatively the following procedure was adopted:—

A solution of the substance in question was prepared of known concentration and its specific gravity determined. This solution was placed in one cell, set to a depth of, say, 21 mm. Some of the same solution was then placed in another cell set to a depth of, say, 1 mm. Light of given known wave-length was then passed through the one solution and the deflection noted. Light of this same wave-length was then passed through the other solution, and the deflection in this case also noted. The deflection produced when the deeper solution was in the path of the beam of light was then divided by the deflection produced when the shallower solution was in the path of the light, and this gave the absolute transmission of the solution of the substance in question of known concentration, having a depth of layer of 20 mm. This process was repeated for the different parts of the spectrum, changing the wave-length of light from reading to reading by only a small amount. Light of any given wave-length was always passed through the one solution, and then at once through the other solution of a different depth. The object in using the two depths of the same solution, and then dividing the deflection produced by the deeper layer by that obtained when the more shallow layer was in the path of the beam of light, was to eliminate any effect of reflection from the glass ends closing the cells containing the solutions, and also to eliminate any changes in the total amounts of energy sent through the solution, due to slight changes in the intensity of the Nernst glower.

From the specific gravity of the solution and its known concentration, the amount of water in a layer of the solution, say, 20 mm. in depth, could easily be calculated. Similarly, the amount of water in a layer of the solution which was 1 mm. deep could also be calculated. Water was then introduced into the two cells, and these cells so adjusted that the difference in the depth of the two was exactly equal to the depth of the water in the layer of the solution which was 20 mm. deep.

The deflection for the water in the deeper cell was then read for any given wave-length of light, and then, at once, the deflection when the light was passed through the *more shallow* layer of water. The deflection for the deeper layer was divided by the deflection for the more shallow layer. This operation was repeated for the various wave-lengths of light in the manner just described. The result was the absolute transmission for water with a depth of layer just equal to the depth of water in the solution in question.

Table I.

λ.	4/N KCl. I/I_0.	H_2O.	4/N NH_4Cl. I/I_0.	H_2O.	3·12/N NH_4NO_3. I/I_0.	H_2O.
710	97	97	92	98	95	98
724	96	95	91	96	97	98
741	95	95	90	92	96	96
760	93	95	85	92	91	95
776	92	95	85	88	92	94
798	94	95	88	95	91	95
818	92	95	87	95	92	96
836	94	93	87	95	91	94
855	91	90	86	93	89	92
878	92	90	86	91	90	93
900	90	89	84	87	89	88
922	87	86	82	86	85	90
947	82	84	79	82	82	83
958	77	78	73	72	73	79
964	75	73	69	70	70	71
969	65	65	64	63	65	67
974	58	56	57	58	58	59
979	51	50	52	52	50	54
982	47	46	45	46	44	46
985	41	45	43	43	40	44
991	39	43	41	43	39	43
1007	39	43	41	42	39	44
1013	40	42	39	44	41	44
1019	42	46	40	46	42	44
1025	41	42	44	49	45	48
1032	49	49	44	49	48	49
1037	53	52	56	55	52	53
1042	56	56	53	58	55	55
1046	59	60	57	57	57	60
1059	63	62	58	65	60	65
1065	68	67	62	67	64	65
1072	71	68	64	68	66	69
1078	74	72	67	67	66	72
1085	75	73	67	66	68	74
1100	77	75	68	72	69	78
1113	76	76	69	72	69	78
1138	75	72	68	70	68	72
1148	70	69	64	65	64	71
1158	64	63	62	64	59	64
1165	58	59	58	58	56	60
1172	52	51	50	50	53	52
1179	42	40	40	40	38	41
1186	29	28	29	26	29	30
1193	18	19	19	19	18	19
1200	13	16	14	13	12	17
1206	10	12	12	12	9	13
1213	10	11	10	12	9	13
1220	10	11	10	11	9	12
1227	10	11	10	11	9	12

The above results for the solution are plotted as one curve, and those for water having the same depth as the water in the solution as another curve, wave-lengths being abscissæ and transmission ordinates. A comparison of the two curves shows at once whether water in the free uncombined condition or the same depth of water in the solution in question is the more transparent.

The data obtained by dividing the deflections produced by the deeper solutions by those for the more shallow, and, similarly, by those for water, are also given in the following tables. These are the data from which the curves were plotted.

The substances studied were chosen from the standpoint of their power to solvate or to combine with the solvent in which they were dissolved. In all of the work recorded in this paper the solvent used was water. We were practically limited, in this phase of the work, to those substances which themselves have little or no power to absorb light. We were limited to those substances that are both colourless in the visible part of the spectrum, and have little or no absorption in the regions in which the absorption bands of water occur.

TABLE II.

λ.	4/N KCl. I/I_0.	H_2O.	4/N NH_4Cl. I/I_0	H_2O.	3·12/N NH_4NO_3. I/I_0.	H_2O.
1085	85	86	79	87	81	88
1100	87	88	80	92	81	93
1113	86	87	79	86	84	86
1138	81	85	79	84	81	84
1148	79	82	77	84	78	84
1158	80	79	74	81	76	81
1165	76	77	71	77	72	77
1172	72	71	66	70	67	70
1179	64	62	59	62	61	62
1186	51	51	52	50	50	50
1193	41	43	42	44	40	44
1200	35	38	37	40	34	40
1206	37	36	35	37	32	37
1213	30	34	30	36	32	36
1220	30	35	29	35	34	35
1227	30	34	30	35	32	35
1233	30	33	28	35	31	35
1241	30	34	29	34	31	34
1248	31	34	28	33	31	33
1250	33	34	30	34	32	34
1255	34	35	30	36	32	36
1268	34	35	31	37	32	37
1270	37	31	32	38	33	38
1285	38	38	33	38	33	38
1295	39	38	32	38	33	38
1300	41	38	32	39	34	39
1308	42	39	32	41	35	41
1316	41	39	32	40	34	40
1323	42	37	32	38	34	38
1330	40	37	32	37	33	37
1338	40	35	30	35	31	35
1346	36	33	28	36	30	36
1352	34	29	26	29	27	29
1358	29	26	23	27	25	27
1365	25	22	21	23	21	23
1372	20	18	17	20	17	20
1387	13	12	12	11	10	11
1404	7	7	7	8	7	8
1418	3	4	4	3	3	3
1430	2	2	3	2	2	2
1445	0	0	0	1	1	1

We selected for these substances with little or no hydrating power salts of potassium and ammonium. The potassium salts studied were the chloride and nitrate. Ammonium chloride and nitrate were also investigated. We selected for the salts with large hydrating power calcium chloride, magnesium chloride, and aluminium sulphate. These salts were shown by the earlier work in this laboratory, which was done shortly after Jones proposed the solvate theory of solutions, using the freezing-point method, to be among the most strongly hydrated substances with which we are familiar.

It will be seen from the following data that two depths of layers of each solution of every substance investigated were employed. The object of this was to bring out the two most important water bands in the region of the spectrum investigated. This could not be done by studying only one depth of solution, since the depth which was necessary and sufficient to bring out clearly one of these water bands would not bring the other out in the way desired. By using the two depths of solution and studying each of them in the manner described above, that is, by the differential method, we were able to investigate both of the water bands as produced, on the one hand, by the pure solvent, and, on the other, by the solution.

In the accompanying tables, under λ are given the wave-lengths of light that were passed through the solution, and under I/I_0 the percentage of transmission, on the one hand, of the solution, and, on the other, of water having a depth exactly equal to that of the water in the solution.

The ordinates of the curve, as has already been state , are percentage transmissions and the abscissæ wave-lengths.

TABLE III.

λ.	5·38/N $CaCl_2$. I/I_0.	H_2O.	4·96/N $MgCl_2$. I/I_0.	H_2O.	1·2/N $Al_2(SO_4)_3$. I/I_0.	H_2O.
710	94	98	95	98	95	93
724	92	98	98	98	95	95
741	90	95	95	98	94	93
760	87	94	94	98	92	93
776	88	93	92	97	93	95
798	91	96	93	94	92	90
818	93	99	90	90	93	92
836	92	97	92	95	92	92
855	90	93	91	90	90	91
878	90	90	91	93	91	90
900	89	92	88	92	89	90
922	86	91	88	91	85	86
947	87	84	84	86	82	81
958	78	79	76	78	76	73
964	75	73	82	76	72	66
969	70	68	75	69	68	61
974	65	62	68	65	64	55
979	59	53	61	56	58	48
982	51	49	48	51	53	42
985	48	49	54	45	51	40
991	44	46	48	49	47	39
1007	42	46	46	48	46	38
1013	42	46	45	50	46	39
1019	43	49	44	51	44	40
1025	47	50	46	44	46	43
1032	52	53	51	54	46	45
1037	55	55	52	56	52	50
1042	58	59	56	58	53	53
1046	62	62	59	65	55	55
1059	66	65	63	67	55	58
1065	71	70	69	70	62	63
1072	74	72	71	75	60	65
1078	75	74	71	76	64	69
1085	78	76	76	79	65	70
1100	80	77	78	79	67	72
1113	79	78	80	81	67	74
1138	77	75	77	78	64	67
1148	74	71	75	77	60	65
1158	69	65	73	73	57	55
1165	66	62	65	65	55	53
1172	61	52	61	58	50	43
1179	54	41	52	44	45	34
1186	42	30	43	32	34	22
1193	32	21	32	24	25	15
1200	22	17	23	18	20	12
1206	16	16	18	17	16	10
1213	13	15	16	18	14	9
1220	12	13	14	15	11	10
1227	12	13	14	16	12	8

In Table I. the depth of layer of all the solutions was the difference between 21 and 1, *i.e.*, 20 mm. The depth of water was in every case the same as that of the water in the solution in question.

The depth of layer of the solutions in Table II. was the difference between 11 mm. and 1 mm., *i.e.*, 10 mm. The depth of water used was in every case the same as that of the water in the solution.

In Table II. the depth of layer of the solution that was used was only half of that in Table I. The object of this was to bring out more prominently the second water band.

The depth of later of the solutions in Table III. was the difference between 21 mm. and 1 mm., *i.e.*, 20 mm. The depth of water used in every case was the same as that of the water in the solution.

In Table IV. the depth of layer used was the difference between 11 and 1 mm., *i.e.*, 10 mm. The object of using the smaller depth of the solution was to bring out more clearly in the case of hydrated salts the second water band.

TABLE IV.

λ.	5·38/N $CaCl_2$. I/I₀.	H_2O.	4·96/N $MgCl_2$. I/I₀.	H_2O.	1·02/N $Al_2(SO_4)_3$. I/I₀.	H_2O.
1085	84	84	82	84	79	82
1100	84	84	83	84	78	81
1113	84	86	83	84	78	84
1138	86	85	82	83	77	83
1148	82	83	79	80	75	80
1158	80	79	77	77	73	77
1165	78	76	77	75	70	73
1172	76	72	74	70	66	69
1179	72	65	71	64	63	58
1186	63	55	62	52	55	48
1193	54	45	56	46	49	39
1200	45	40	48	43	43	34
1206	38	39	42	40	38	30
1213	35	39	39	38	36	29
1220	33	36	[illegible]	38	34	28
1227	32	36	36	38	32	28
1233	31	35	34	37	32	28
1241	32	35	34	34	31	28
1248	32	35	34	37	31	28
1250	33	35	34	38	31	28
1255	33	37	34	38	31	28
[illegible]	35	38	33	38	30	29
1270	37	39	34	39	30	30
1285	38	40	35	40	30	31
1295	40	40	35	40	30	32
1300	42	41	36	41	30	32
1308	42	41	37	42	30	33
1316	45	41	39	42	30	33
[illegible]	47	40	39	41	28	33
[illegible]	45	39	40	40	27	32
[illegible]	45	37	38	38	27	30
[illegible]	42	35	38	36	24	27
1352	40	32	34	33	22	24
1358	37	29	33	30	20	21
1365	33	25	29	26	18	19
1372	29	21	25	22	15	15
1387	19	13	18	15	10	9
1404	12	10	12	11	7	5
1418	7	6	7	9	4	3
1430	3	3	4	3	2	2
1445	2	1	1	1	1	1

(To be continued).

THE SCIENTIFIC WEEK.

(From Our Paris Correspondent).

SUGAR MAY STOP THE DEVELOPMENT OF YOUNG SUBJECTS.

MM. Jacques Parisot and Pierre Mathieu have arrived at the following conclusions after having subjected a certain number of rabbits to the ingestion of sugar for periods varying from a few weeks to several months:—

At first a decrease of weight is observed, soon followed by a recovery or even an increase, then finally a persistent decrease. The troubles caused by the first ingestions are pretty easily reparable, those resulting from the absorption of abundant and repeated doses are much more lasting. Lastly, the animals experimented upon feel indefinitely the effects of this obstacle thus opposed to their development.

These are but laboratory experiments, effected on animals, and their results, naturally, could not, uncontrolled, be applied to human beings. Nevertheless, they are worth taking into consideration, and it would be advisable to have but a limited confidence in the alimentary value of sugar whenever it is absorbed in considerable quantities.

THE WATERING OF THE LAND.

It is well known how much the watering of the ground increases the production of the crops as well as the value of the land. Generally water only exists in insufficient quantities, and it is necessary not to waste it, so as to make it go over as large a space as possible.

In their studies MM. Mintz and Lainé have discovered that generally too much water is employed, and that it might be economised without diminishing the effects of irrigation. This water might then be employed over larger surfaces.

The two chemists have determined the quantities of water really useful for grounds of different kinds. These quantities vary enormously. MM. Mintz and Lainé have also fixed the data of a rational arrangement which would realise a great economy of water.

EXTRACTION OF OIL FROM CONDENSATION WATER.

The escapement vapour of steam engines draws off, mechanically with itself, the greasing oil, and this has induced engineers to construct different apparatus for the extraction of this oil. But ordinary separators only retain about 75 per cent; the 25 per cent which remains go into the condenser, where they produce in the water little spheric corpuscles, a veritable emulsion as it were, which forms a layer on the surface of the water. This layer presents the particularity of being electrically charged and acts like a veritable colloidal solution.

It is then possible by the addition of a colloidal solution, charged with electricity of a contrary sign, to produce the precipitation of the oil. This is what takes place in a new process that consists in electrolysing the water by the help of electrodes of iron after having rendered it conductive by a dissolution of carbonate of soda.

It is thus possible to eliminate 98·5 per cent of the oil, and the expense for the electric current and the carbonate of soda does not exceed five centimes (one half-penny) per cubic metre treated. Moreover, the small quantity of alkali that remains in the water is advantageous, as it has the effect of delaying the attack on the iron of the walls of the cauldron.

THE FORECAST OF STORMS BY WIRELESS TELEGRAPHY.

M. Turpain, Professor at the Faculty of Science of the University of Poitiers, continues to pursue his experiments concerning the forecast of storms by wireless telegraphy.

The observations, registrations, and forecasts of storms have, says M. Turpain, been pursued throughout the year 1912 by means of different arrangements of apparatus that I described last year, principally by means of receptive apparatus with needles, inserted in the circuit of an enregistrating milli-ampèremeter. These apparatus have been worked at the posts of Poitiers (Faculty of Sciences, Manroc, University of Poitiers), La Rochelle, Paris-la-Nation, the Observatory of the Pic du Midi, Bagnères de Bigorre, the Observatory of the Puy de Dôme.

The forecast was currently from four to five hours, and sometimes reached six to eight hours.

The station installed in Paris, Place de la Nation, has been able to warn the farmers of Montreuil and to avoid them having firing to prevent hail storms, either when the weather although threatening was not stormy, or when it was deduced from the inscription that the storm would not pass over Montreuil. In this way, with a saving of L. 8 for every firing avoided, the Paris station was able to make the Montreuil part economise several thousand francs.

The same apparatus are employed at the Bordeaux Observatory for the control of the para-hail apparatus installed in the department of Gironde.

Besides these indications of a practical order, the indications supplied by the foretellers allow of great precision in the meteorological data. Thus, at the Observatory of Bagnères de Bigorre most valuable information has been deduced concerning the prevision of the weather. At Paris-la-Nation stormy weather has been foretold successfully several times [illegible] hours in advance.

The studies made with a view of foreseeing rain or a rainy period have been pursued, and have given a concordance of about 75 per 100. These researches are especially to be pursued with bolometric apparatus allowing of the enregistering of the energy of the discharges. In order to confirm these new results it is necessary to undertake new bolometric measures simultaneously in two posts of observation.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, June 26th, 1913.

Sir Ronald Ross, K.C.B., Vice-President, in the Chair.

Papers were read as follows:—

"*Phosphorescence of Mercury Vapour after Removal of the Exciting Light.*" By F. S. Phillips.

"*Light Sensations and the Theory of Forced Vibrations.*" By Dr. G. J. Burch, F.R.S.

"*Fluctuation in the Ionisation due to γ-Rays.*" By P. W. Burbidge.

"*Force Exerted on a Magnetic Particle by a varying Electric Field.*" By J. G. Leathem, M.A.

"*Luminosity Curve of a Colour-Blind Observer.*" By W. Watson, F.R.S.

"*A Critical Study of Spectral Series.* Part III. *The Atomic Weight Term, and its Import in the Constitution of Spectra.*" By Prof. W. M. Hicks, F.R.S.

"*A Band Spectrum Attributed to Carbon Monosulphide.*" By L. C. Martin.

A complex band system occurring in the spectrum of the electric discharge through carbon disulphide vapour in addition to the bands due to sulphur, is also found in the spectrum given by sulphur in the carbon arc. These bands only occur in the presence of both sulphur and carbon, and are probably due to carbon monosulphide.

"*Structure of the Skull of Dicynodon as Revealed by Serial Sections.*" By Igerna B. J. Sollas and W. J. Sollas, F.R.S.

"*Carbohydrate-metabolism in its Relation to the Thyroid Gland.—The Effect of Thyroid Feeding on the Glycogen Content of the Liver and on the Nitrogen Distribution in the Urine.*" By W. Cramer and R. A. Krause.

"*Sublimation of Metals at Low Pressures.*" By G. W. C. Kaye, D.Sc., and D. Ewen.

"*Energy of Röntgen Rays.*" By R. T. Beatty, D.Sc.

"*Some Phenomena of Sunspots and of Terrestrial Magnetism.*" Part II. By Dr. C. Chree, Sc.D., LL.D., F.R.S.

The paper is a continuation of one termed for brevity S.M., which appeared in the *Phil. Trans.*, A, ccxii., 75. It is mainly devoted to the question of the existence of a period of approximately twenty-seven days in terrestrial magnetic phenomena. Independent studies of magnetic storms during a very long period of years at Greenwich and Toronto led Mr. Harvey and Mr. Maunder a good many years ago to the conclusion that an interval of about twenty-seven and a-quarter days could be recognised between the commencements of successive magnetic storms in a greater number of cases than could reasonably be ascribed to pure chance. S.M. showed that whether one took the daily range of horizontal force at Kew, or the magnetic character of the day, there undoubtedly existed for the epoch 1890 to 1900 a period of twenty-seven days or slightly more, in the sense that if an individual day were highly or moderately disturbed, days twenty-seven or twenty-eight days later were on the average more disturbed than usual. The result was not peculiar to the large disturbance usually termed "magnetic storms," and appeared in all the years examined, whether quiet or disturbed.

The present paper finds the same result to hold true of the years 1906 to 1911 when use is made of the magnetic "character" figures which have been published since 1906 at de Bilt, under international auspices. It is also found that the result is as true of quiet as of disturbed characteristics. If an individual day is quiet, the day which is twenty-seven or twenty-eight days subsequent is on the average more quiet than normal. Moreover, whether the selected day is quiet or disturbed, the days which are earlier by twenty-seven or twenty-eight days show a relation to it exactly similar in character and amount to that shown by the day which is twenty-seven or twenty-eight days subsequent. The relation can also be traced both backwards and forwards in time for several successive multiples of the twenty-seven-day period, the amplitude of the successive "pulses" gradually diminishing.

The paper also investigates whether the phenomena presented by the twenty-seven day period vary with the period of the year, and what the relationships are, if any, between magnetic "character" and Greenwich measures of sunspot area and faculæ and Wolfer's sunspot frequencies. The apparent sunspot relationships are found to vary a good deal from year to year.

"*New Series of Lines in the Spark Spectrum of Magnesium.*" By A. Fowler, F.R.S.

From experiments on the spectrum of the magnesium arc *in vacuo*, it has been found that there are seven lines which are associated with the well-known spark line 4481·35, their wave-lengths being 3104·91, 2661·00, 2449·68, 2329·68, 2253·94, 2202·75, and 2166·35. The eight lines, taken alternately, fall into two series having their common limit at 49776 on the frequency scale. The series are analogous to the two principal series of hydrogen lines, which have recently been investigated by the author.

"*Additional Triplets and other Series Lines in the Spectrum of Magnesium.*" By A. Fowler, F.R.S., and W. H. Reynolds, B.Sc.

The paper gives particulars of eight new triplets which have been photographed in the ultra-violet spectrum of magnesium, and improved wave-lengths for some of the lines previously recorded. The Rydberg series of single lines has also been extended, and four strong solar lines of previously unknown origin have been identified with lines of this series. Attention is also drawn to a probable second subordinate series of single lines. Formulæ representing the various series are given.

"*A New Band Spectrum Associated with Helium.*" By W. E. Curtis, B.Sc.

The paper describes a new band spectrum observed under certain conditions in vacuum tubes containing helium and hydrogen. The experiments suggest that the bands are due to helium, but until hydrogen can be more completely eliminated their origin cannot be regarded as definitely settled.

"*A Case of Abnormal Trichromatic Colour Vision Due to a Shift in the Spectrum of the Green Sensation Curve.*" Sir W. De W. Abney, F.R.S., and W. Watson, F.R.S.

"*Studies on the Processes Operative in Solutions (XXX.) and on Enzyme Action (XX.). The Nature of Enzymes and of their Action as Hydrolytic Agents.*" By E. F. Armstrong and Prof. H. E. Armstrong, F.R.S.

"*Studies on Enzyme Action.*" XXI. *Lipase.*" III. By Prof. H. E. ARMSTRONG, F.R.S., and H. W. GOSNEY, B.Sc.

"*Studies in the Heat Production Associated with Muscular Work.*" (Preliminary Communication). By Prof. J. S. MACDONALD.

"*Formation of the Anthocyan Pigments of Plants.*" Part VI. By Prof. F. KEEBLE, F.R.S., E. F. ARMSTRONG, D.Sc., and W. N. JONES.

"*Question of Fractional Activity ('All or None' Phenomenon) in Mammalian Reflex Phenomena.*" By T. GRAHAM BROWN.

"*Thermal Effects Produced by Heating and Cooling Palladium in Hydrogen.*" By J. H. ANDREW and A. HOLT, D.Sc.

"*Peculiar Form of Low Potential Discharge in the Highest Vacua.*" By HON. R. J. STRUTT, F.R.S.

"*Note on Copying Machinery.*" By A. MALLOCK, F.R.S.

"*Relation between the Crystal-symmetry of the Simpler Organic Compounds and their Molecular Constitution.*" Part II. By WALTER WAHL.

"*Experiments on the Temperature Coefficient of a Kew Collimator Magnet.*" By G. A. SHAKESPEAR.

"*Spectroscopic Investigations in Connection with the Active Modification of Nitrogen.* III. *Spectra Developed by the Tetrachlorides of Silicon and Titanium.*" By W. JEVONS.

"*Passage of Waves through Fine Slits in thin Opaque Screens.*" By LORD RAYLEIGH, O.M., F.R.S.

"*Reflection of X-rays by Crystals.*" II. By Prof. W. H. BRAGG, F.R.S.

In a previous communication (April, 1913) it was shown that the wave-lengths of homogeneous pencils of X-rays could be expressed accurately in terms of the space relations of a crystal. The formula $\lambda = 2d \sin \theta$ connected the wave-length λ with θ, the glancing angle at which the pencil was reflected in the crystal face, and d the distance between parallel reflecting planes. The angle θ could be determined with accuracy, but want of exact knowledge of crystal structure threw difficulties in the way of a complete evaluation of wave-length. W. L. Bragg, using two independent methods of research (those of the Lane diagram, and of reflection in the crystal face), has shown that in all probability the value of d is $2{\cdot}81 \times 10^{-8}$ cm. From this it follows that the wave-length of the "B peak" is $1{\cdot}10 \times 10^{-8}$. Characteristic radiations having wave-lengths $1{\cdot}25 \times 10^{-8}$ and $1{\cdot}66 \times 10^{-8}$ are emitted by bulbs having anticathodes of tungsten and nickel respectively. So far as it has been found possible to measure the absorption coefficients, they belong to rays which are characteristic of the anticathode metals, and the quantum energy—Planck's constant multiplied by frequency—agrees well with the energy of the cathode ray which, according to Whiddington, is required to excite the X-ray, or which the X-ray can excite.

"*Structure of some Crystals as Indicated by their Diffraction of X-rays.*" By W. L. BRAGG.

An analysis of the Lane diagram of sylvine (KCl) shows that the diffracting centres are arranged on a space lattice of the simplest cubicle form. The diagrams of potassium iodide and bromide show that the diffracting centres are arranged on a lattice whose element is the face-centred cube. Sodium chloride is an intermediate case. From this and other features of the diagrams, it is concluded that in all these crystals the atoms of metal and halide are arranged in a simple cubic lattice, rows parallel to the axes containing alternate atoms of either kind. In sylvine the equal weights of the atoms render them equally efficient as centres; in KBr and KI the heavy halogen atoms alone act, and so the pattern is characteristic of the face-centred cube lattice. The diagrams of other crystals are discussed in reference to these conclusions.

By means of the X-ray spectrometer, described in a previous paper, the dimensions of these lattices can be accurately compared; and the relative magnitudes of the different orders of spectra reflected from any face, and from different crystals, yield information which confirms the above conclusions. It also appears that the weight associated with each point of the lattice is proportional to the molecular weight of the substance. These conclusions yield the necessary information for the accurate calculation of the wave-length of the X-ray.

"*Resonance of the Tissues as a Factor in the Transmission of the Pulse and in Blood Pressure.* By LEONARD HILL, F.R.S., J. M. MCQUEEN, and W. W. INGRAM.

"*Experiments on the Flow of Viscous Fluids through Orifices.*" By G. F. DAVIDSON.

CHEMICAL SOCIETY.

Ordinary Meeting, June 19th, 1913.

Prof. W. H. PERKIN, LL.D., F.R.S., President, in the Chair.

(Concluded from p. 21).

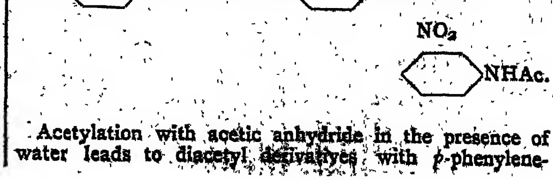
206. "*Influence of Substitution on the Reactivity of* p-*phenylenediamine.*" By GILBERT T. MORGAN and JOSEPH ALLEN PICKARD.

This investigation, which is a contribution to the study of the inhibition of chemical change, was initiated with the object of ascertaining the part played by substituents in modifying the reactivity of *p*-phenylenediamine and its homologues. The following preliminary experiments were carried out on two derivatives of this diamine containing negative substituents.

I. *The Reactivity of Nitro-*p-*phenylenediamine.*

1. *Acetylation.*—One acetyl group only was introduced into the molecule of this nitrodiamine by suspending the base in water, adding excess of acetic anhydride, and subsequently heating to boiling. The product, which crystallised from water in light red, felted needles, melting at 189°, was identical with the monoacetyl derivative previously obtained by half hydrolysing nitrodiacetyl-*p*-phenylenediamine with ammonia, dilute aqueous alkalis, or preferably with baryta water (*Ber.*, 1884, xvii., 148; 1886, xix., 339; 1897, xxx., 980; 1903, xxxvi., 415).

As the constitution of this compound has been assumed without proof, it was dissolved in cold alcohol and treated successively with hydrogen chloride and nitrous fumes, the diazonium chloride being precipitated with dry ether. This salt was suspended in absolute alcohol, the mixture warmed with copper powder, and the solution neutralised with calcium carbonate, filtered, and evaporated nearly to dryness. *m*-Nitroacetanilide (m. p. 150°) separated, and was further identified by hydrolysis to *m*-nitroaniline (m. p. 112°). These reactions fix the constitution of the acetyl derivative as 2-*nitro*-4-*acetyl*-p-*phenylenediamine*,—



Acetylation with acetic anhydride in the presence of water leads to diacetyl derivatives with *p*-phenylene-

diamine and its homologue, 2 : 5 tolylenediamine; it is also practicable with *m*- and *p*-nitroanilines, but not with *o*-nitroaniline.

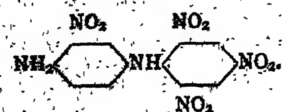
2. *Picrylation.*—Only one picryl group is introduced by boiling nitro-*p*-phenylenediamine for twelve hours with excess of picryl chloride (3 mols.) in dry toluene over anhydrous sodium acetate.

Nitro-4-picryl-p-phenylenediamine, which separated in dark red crystals melting at 255°, dissolved in aqueous or alcoholic sodium hydroxide, and was only sparingly soluble in alcohol, glacial acetic acid, or concentrated hydrochloric acid:—

0·2028 gave 39·1 cc. N_2 at 15° and 766 mm. N = 22·77.
$C_{12}H_8O_8N_6$ requires N = 23·10 per cent.

Comparative experiments with *o*-nitroaniline and 2 : 4-dinitroaniline showed that these bases are not picrylated under the foregoing conditions, and it is accordingly highly probable that in nitro-*p*-phenylenediamine picrylation occurs in the amino-group remote from the nitro-radicle. Direct evidence was obtained by dissolving the picryl derivative in concentrated sulphuric acid and adding successively to the bright yellow solution nitrosyl sulphate and alcohol, the temperature being kept below 5°. The solution of diazonium sulphate thus produced gave a deep red azo-β-naphthol derivative, dissolving in concentrated sulphuric acid to a bluish green solution.

When boiled with copper powder, the alcoholic solution of the diazonium salt evolved nitrogen, and yielded picryl-*m*-nitroaniline (m. p. 207°), thus indicating the following constitution for the picrylated diamine:—



3. *Diazotisation.*—Although nitro-*p*-phenylenediamine diazotises most readily to the monodiazonium salt (Bülow, *Ber.*, 1896, xxix., 2285) in 50 per cent sulphuric acid, the second amino-group is attacked, with the production of the bisdiazonium sulphate. These reactions have been turned to account in the preparation of 4-nitro-*m*-toluidine. The homologous base, 4-nitro-2 : 5 tolylenediamine, behaved in a similar manner, diazotising chiefly to 4-nitro-5-aminotoluene-2-diazonium chloride with a smaller proportion of 4-nitrotoluene-2 : 5-bisdiazonium chloride.

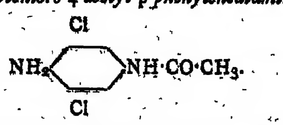
II. *The Reactivity of 2 : 6-Dichloro-p-phenylenediamine.*

1. *Acetylation.*—When boiled with acetyl chloride, 2 : 6 dichloro-*p*-phenylenediamine yielded 2 : 6-*dichlorodiacetyl-p-phenylenediamine*, which crystallised from alcohol or hot water in colourless needles, melting at 253—254°:—

0·1722 gave 15·4 cc. N_2 at 12° and 757 mm. N = 10·5.
$C_{10}H_{10}O_2N_2Cl_2$ requires N = 10·73 per cent.

When boiled for fifteen minutes with N-sodium hydroxide solution (30 parts), the diacetyl derivative yielded a monoacetyl compound, crystallising from alcohol in lustrous, colourless plates, melting at 218°, and dissolving in dilute hydrochloric acid, the soluble hydrochloride being readily diazotised.

2 : 6-*Dichloro-4-acetyl-p-phenylenediamine*,



This isomeric monoacetyl derivative was produced by shaking 2 : 6-dichloro-*p*-phenylenediamine with excess of acetic anhydride and water. It crystallised from alcohol or water in colourless needles, melting at 200°:—

0·1553 gave 17·3 cc. N_2 at 18° and 759 mm. N = 12·85.
$C_8H_8ON_2Cl_2$ requires N = 12·70 per cent.

The constitution of this compound was determined by adding nitrosyl sulphate to its slightly warm solution in absolute alcohol. The diazonium sulphate, which separated in colourless, feathery needles, was suspended in alcohol and treated with copper powder, when a brisk evolution of nitrogen occurred. 3 : 5-Dichloroacetanilide (m. p. 187°) separated in colourless crystals on diluting the filtered solution with water, and this product, when hydrolysed with concentrated hydrochloric acid, yielded 3 : 5-dichloroaniline (m. p. 51°).

2. *Picrylation.*—Only one amino-group is picrylated on boiling 2 : 6-dichloro-*p*-phenylenediamine with picryl chloride in toluene solution over anhydrous sodium acetate.

2 : 6-*Dichloropicryl-p-phenylenediamine*,

$$NH_2{\cdot}C_6H_2Cl_2{\cdot}NH{\cdot}C_6H_2(NO_2)_3,$$

separated from glacial acetic acid in lustrous, dark red crystals, sintering at 220° and melting at 227—228°:—

0·1516 gave 0·1119 AgCl. Cl = 18·25.
$C_{12}H_7O_7N_5Cl_2$ requires Cl = 18·27 per cent.

The compound was soluble in aqueous or alcoholic alkali hydroxides, but dissolved only very sparingly in hydrochloric acid.

3. *Diazotisation.*—2 : 6-Dichloro-*p*-phenylenediamine did not diazotise smoothly in aqueous solutions of the mineral acids, and although the reaction proceeded more readily in alcoholic or glacial acetic acid solution, even then only one amino-group was diazotised with the formation of 2 : 6-dichloro-1-aminobenzene-4-diazonium chloride or sulphate. On treatment with absolute alcohol and copper powder, these diazonium salts yielded 2 : 6-dichloroaniline, thus showing that the amino-group diazotised is the one in the meta-position with respect to the chlorine atoms.

Summary.

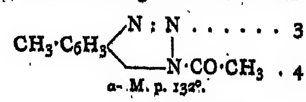
1. The introduction of a negative radicle into the aromatic nucleus of *p*-phenylenediamine hinders very considerably the acetylation of the amino-group contiguous to this substituent. The picrylation of this amino-group is completely inhibited.

2. The introduction of one nitro-group into the *p*-phenylenediamine or 2 : 5-tolylenediamine nucleus diminishes very considerably the diazotisability of the contiguous amino-group. The presence of two chlorine atoms in ortho-positions with respect to one amino-group of *p*-phenylenediamine inhibits completely the diazotisation of this group.

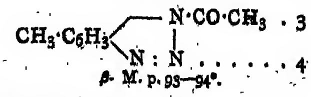
207. "*The Constitution of the Ortho-diazoimines.* Part III. *The α- and β Acyl-3 : 4-Tolylenediazoimides as Structural Isomerides.*" By Gilbert T. Morgan and Francis Mary Gore Micklethwait.

3 : 4-Tolylenediazoimine or its metallic derivatives yield on acetylation a mixture of two acetyl derivatives, which have hitherto been regarded as "physical isomerides" (Zincke and Lawson, *Ann.*, 1887, ccxl., 119).

The authors have shown that these compounds are structural isomerides having the constitutional formulæ:—



α- M. p. 132°.

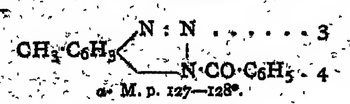


β- M. p. 93—94°.

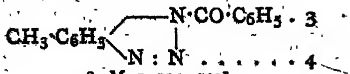
arising respectively as sole products of the diazotisation of 4-acetyl-3 : 4-tolylenediamine and 3-*acetyl*-3 : 4-*tolylenediamine*.

The chemical nature of the foregoing case of isomerism was confirmed by obtaining from 4-benzoyl-3 : 4-tolylenediamine and 3-*benzoyl*-3 : 4-*tolylenediamine* respectively, the isomeric pair of *benzoyl*-3 : 4-*tolylenediazoimides*

having constitutions represented by the following formulæ:—



α- M. p. 127—128°.



β- M. p. 122—123°.

The existence of these two pairs of isomerides affords additional confirmation of Kekulé's formula for diazoimines as opposed to the configuration of these diazo-derivatives advocated by Griess.

208. "*The Occurrence of Neon in Vacuum-tubes Containing Hydrogen.*" By Irvine Masson.

Experiments are in progress to test further the results of Collie and Patterson (*Trans.*, 1913, ciii., 419), and have yielded independent evidence of the fact that neon appears after the passage of an electrical discharge through a vessel containing a gas previously free from neon.

When pure dry hydrogen was sparked in a discharge-tube bearing a perforated aluminium disk cathode and having a vacuous jacket surrounding it, it was found that after a time a neon ceased to be formed; on then admitting a mixture of oxygen and hydrogen and passing the discharge, the tube appeared to be rendered "active" once more, for thereafter neon was steadily produced when hydrogen was sparked.

In all these experiments, hydrogen accumulated in the initially vacuous jacket, and had apparently passed through from the discharge-tube. Quantities up to about one-third of a cc. could be so obtained. This gas was found to contain no other, except carbon-monoxide in small and varying amounts.

209. "*A Simple and Efficient Method of Dehydrating Substances by Electrical Heating in a Vacuum.*" By William Ernest Stephen Turner and Crellyn Colgrave Bissett.

Methods of electrical heating within a vacuum desiccator have already been described by Skita (*Chem. Zeit.*, 1902, xxvi., 898) and by Scheermesser (*Ibid.*, 1903, xxvii., 175). The first-named author used two 16-candle-power lamps promoting a temperature of 70°; the second, a plate; and both methods are suitable more for the evaporation of liquids than for dehydration at higher temperatures.

The author's own method, which was in use some time before they were aware of previous arrangements, is not only much more efficient, but also far simpler. It consists in introducing into a vacuum desiccator a heating coil made of manganin wire, a length of 90 cm. of No. 20 wire gauge being very suitable, so as to give a coil of about 4 cm. internal diameter. A cover for the coil is made by wrapping round it a strip of asbestos paper, previously moistened. Connexion is made with the coil by two leads of stout copper wire, which pass through two pieces of narrow quill glass tubes inserted in the rubber stopper of the desiccator, the upper ends of the glass tubes being then closed by sealing wax.

Using a small platinum dish, weighing 12 grms., 3·5 grms. of powdered silica were maintained in the exhausted desiccator at a temperature of 36° with a current of 2 amperes, 92° with 4 amperes, and 154° with 5·8. Still higher temperatures may be reached if desired. The drying agent used in the desiccator is phosphoric oxide.

The value of the method will be realised by the two following cases, in which dehydration by previous methods appears to have been both difficult and not entirely successful.

Lithium iodide at the ordinary temperature occurs as the trihydrate, although the commercial samples are usually partly dehydrated. In Abegg's "Handbuch der anorganischen Chemie," vol. II., p. 130, it is stated that the anhydrous form may be produced by heating above 300°, but that the substance so obtained is not pure, since at this temperature it attacks glass and porcelain. From the authors' tests, a sample of the salt of composition corresponding precisely with the monohydrate did not lose moisture by standing over phosphoric oxide in an exhausted desiccator for three weeks. By the new process, pure anhydrous lithium iodide (Found, I = 94·9. Calc., I = 94·8 per cent.) was obtained after raising the temperature to about 100° for several hours. The iodide so obtained is quite white.

Rhamnose is another substance the dehydration of which up to now has proved very difficult. It occurs ordinarily combined with one molecule of water, and its dehydration not only requires prolonged heating on a water-bath, but the process is also accompanied by at least a partial conversion into the β-form. Purdie and Young (*Trans.*, 1906, lxxxix., 1194) state that dehydration is incomplete after prolonged heating at 70—90° under diminished pressure and in presence of phosphoric oxide, and is accompanied in this case also by partial conversion into the β-form. The authors have been successful in completely dehydrating rhamnose during the course of a week by raising the temperature within the exhausted desiccator very slowly to about 90°. Moreover, polarimetric observations (made by Mr. C. R. Young) point to the absence of the β-form from the dehydrated sugar.

210. "*The Vapour Density of Ammonium Nitrate, Benzoate, and Acetate.*" By Prafulla Chandra Ray and Sarat Chandra Jana.

A detailed description of work of which a preliminary account has already appeared (*Proc.*, vol. xxix., p. 28).

211. "*The Action of Nitric Oxide on a Neutral Solution of Potassium Permanganate.*" By Barum Chandra Dutt, Bamacharan Chatterji, and Haridas Banerji.

When nitric oxide is passed through a solution of potassium permanganate in an atmosphere of hydrogen, the reaction which takes place is represented by the equation $KMnO_4 + NO = KNO_3 + MnO_2$.

There is no intermediate formation of nitrous acid.

NOTICES OF BOOKS.

A Dictionary of Applied Chemistry. By Sir Edward Thorpe, C.B., LL.D., F.R.S. Assisted by Eminent Contributors. Revised and Enlarged Edition. Vol. IV. Oilstone to Soda Nitre. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1913.

The fourth volume of the new edition of this valuable dictionary contains some very lengthy and highly important articles on subjects of great technical interest; for example, rubber, petroleum, paints, &c., while the more purely scientific side of the subject is given adequate consideration. The names of the contributors include those of the best known experts in every branch of applied chemistry, and the fourth volume is in every respect fully up to the level of its predecessors.

Manual of Qualitative Analysis. By Wilbur F. Hoyt, A.B., A.M. New York: The Macmillan Co. 1913.

The methods generally employed in the qualitative analysis of inorganic compounds are briefly described in this small book, which is characterised by great conciseness. Wet tests for the commoner metals and acid radicles are given in the most condensed form possible, and all difficult equations are group together, while the simpler are given in the descriptions of the tests. Some notes on valence and the

writing of equations are added, and a few simple tests for the examination of drinking water are included. Dry tests are described in the later parts of the book, and it is recommended that their application should be deferred until the student is doing his second year's work in the laboratory, a plan which is not usually regarded as advisable.

Liquid Air, Oxygen, Nitrogen. By GEORGES CLAUDE. Translated by HENRY E. P. COTTRELL. London: J. and A. Churchill. 1913.

THIS translation will be much appreciated in England, where for some time the need has been felt of an authoritative and comprehensive standard work on the liquefaction of gases and the use of liquid air. The author has done some valuable pioneering work on the subject, and his experiments have done much to further the liquid air industry. The book is written in a very interesting and graphic style, and gives a detailed description of the early experiments which led up to the liquefaction of the so-called permanent gases and of the chief processes for the commercial preparation of liquid air. The properties of liquid air are fully discussed, many striking experiments which can be performed with it being outlined, while some remarkable illustrations are included. The separation of the air into its elements and the cheap manufacture of oxygen on a large scale are treated in Part IV., and some installations of different systems in Germany and France are described. Theoretical considerations are by no means neglected, and the book provides an admirable survey of the theory and practice of the liquefaction of air.

Chloride of Lime in Sanitation. By ALBERT H. HOOKER. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1913.

THE research department of the Hooker Electrochemical Company, on the advice of Dr. L. H. Baekeland, President of the American Institute of Chemical Engineers, recently undertook to collect all available data relating to the use of chloride of lime in sanitation, and the amount of material brought together was so large and appeared of such great value that it was decided to publish it in book form. Sanitary officials in this country should be grateful for this decision, more particularly as the book contains short abstracts of a large number of articles on sanitation which have appeared in various journals and which are referred to in the text. These abstracts are arranged under convenient headings and the book is well indexed. For its treatment of the subject of the campaign against the house fly alone it is an important contribution to the literature of sanitation which should be in the hands of all who are in charge of work connected with the public health.

Jahrbuch der Organischen Chemie. ("Year Book of Organic Chemistry.") By Professor Dr. SCHMIDT. Sixth year. Leipzig: Johannes Wörner. 1913.

A DETAILED survey of the progress in organic chemistry made during the year 1912 is given in this book. In the first and general section the important work which has been done on the stereo-chemistry of carbon and nitrogen is summarised, and Wörner's work on the isomerism of Co, Rh, Cr, and Fe compounds is discussed. The study of the physical properties or organic compounds has recently made considerable advances, and the work of K. v. Auwers and others appears to be leading to important developments, as is duly pointed out. In the special part the many new syntheses which have been effected are described as well as experiments which have thrown light upon the constitution of important compounds. The chemistry of chlorophyll is discussed at some length and also the preparation of synthetic rubber. The year book contains a list of works on organic chemistry which were published in the German language during the year 1912, and also a few short obituary notices.

Directory of Paper Makers of the United Kingdom for 1913. London: Marchant, Singer, and Co.

THE 1913 edition of the Paper Makers' Directory has been thoroughly revised and numerous additions have been made to the list of trade designations. A complete catalogue of actual watermarks is given, and another of trade names which are not watermarks. In addition the directory contains some short notes on paper trade customs.

CORRESPONDENCE.

CHROMATE AND BICHROMATE OF POTASSIUM OR SODIUM.

To the Editor of the Chemical News.

SIR,—I am directed by the Secretary of State to transmit to you herewith a copy of a draft of Regulations which he proposes to make under Section 79 of the Factory and Workshop Act, 1901, for the manufacture of chromate and bichromate of potassium or sodium.—I am, &c.

H. W. ROBINSON,
Deputy Chief Inspector of Factories.

Home Office, July 9, 1913.

Definitions.

(Terms to which defined meanings are given are printed throughout the Regulations in italics).

In these Regulations:—

"*Chrome process*" means manipulation, movement, or other treatment of chromate or bichromate of potassium or sodium.

"*Surgeon*" means the Certifying Factory Surgeon of the district or a duly qualified medical practitioner appointed by written certificate of the Chief Inspector of Factories, which appointment shall be subject to such conditions as may be specified in that certificate.

"*Suspension*" means suspension from employment in any *chrome process* by written certificate in the Health Register, signed by the *Surgeon*, who shall have power of *suspension* as regards all persons employed in any *chrome process*.

"*Efficient exhaust draught*" means localised ventilation effected by heat or mechanical means, for the removal of steam or dust so as to prevent them from escaping into the air of any place in which work is carried on.

Duties.

It shall be the duty of the occupier to observe Part I. of these Regulations.

It shall be the duty of every person employed to observe Part II. of these Regulations.

Part I.—Duties of Occupiers.

1. With regard to every uncovered fixed vessel, whether pot, pan, vat or other structure, containing any corrosive liquid.

(*a*) Each such vessel shall, unless its edge is at least 3 feet above the adjoining ground or platform, be securely fenced;

(*b*) For the purposes of paragraph (*a*) of this Regulation no fencing shall be deemed to be secure unless it extends to a height of at least 3 feet above the adjoining ground or platform: provided however that Paragraph (*b*) of this Regulation shall not apply:—

(i.) to any vessel constructed before 1st January, 1899; or

(ii.) where a height of 3 feet is impracticable by reason of the nature of the work to be carried on;

(c) No plank or gangway shall be placed across any such vessel unless such plank or gangway is—
(i.) at least 18 inches wide; and
(ii.) securely fenced on both sides; either by upper and lower rails, to a height of 3 feet, or by other equally efficient means;

(d) Where such vessels adjoin, and the space between them either—
(i.) affords foothold, and is not fenced as in paragraph (c) (ii.) of this Regulation, or
(ii.) is less than 18 inches in width, clear of any brick or other work surrounding them,
a secure barrier shall be so placed as to prevent passage between them.

2. All dangerous places near to which persons are employed, or near to which they have to pass, shall be efficiently lighted by day and night.

3. Grinding, unless done with slow moving edge runners, and sieving the raw materials, evaporating, and packing shall not be carried on except either—
(a) with an *efficient exhaust draught;* or
(b) in such manner as will prevent escape of dust or fume into the air of any place at which work is carried on.

4. No person under eighteen years of age and no female shall be employed in any *chrome process*.

5.—(a) Every person employed in a *chrome process* shall be examined by the *Surgeon* once in every calendar month on a date, or dates, of which due notice shall be given. The *Surgeon* shall undertake any necessary medical treatment of lesions contracted in consequence of such employment.

(b) A Health Register containing the names of all persons employed in any *chrome process* shall be kept in a form approved by the the Chief Inspector of Factories.

(c) No person after *suspension* shall be employed in any *chrome process* without written sanction from the *Surgeon*, entered in the Health Register.

6. Requisites (approved by the *Surgeon*) for treating slight wounds and ulcers shall be kept at hand and be placed in charge of a responsible person.

7. There shall be provided—
(a) sufficient and suitable overall suits for the use of all persons engaged in grinding the raw materials, which overall suits shall be washed, cleaned, or renewed at least once every week; and
(b) sufficient and suitable protective coverings for the use of all persons engaged in the crystal department and in packing;

8. There shall be provided suitable respirators for the use of all persons employed in packing bichromate of potassium or sodium; which respirators shall be washed or renewed at least once every day.

9. There shall be provided and maintained for the use of all persons employed in any *chrome process*—
(a) a suitable meal room;
(b) a suitable place or places for clothing put off during working hours; and
(c) a suitable place or places for the storage of overall suits provided in pursuance of Regulation 7 (a); which place or places shall be separate from that required by paragraph (a) of this Regulation.

10. There shall be provided and maintained in a cleanly state and in good repair for the use of all persons employed in any *chrome process*—
(a) a lavatory, under cover, with a sufficient supply of clean towels, renewed daily, and of soap and nail brushes, and with either—
(i.) a trough with a smooth impervious surface fitted with a waste-pipe, without plug, and of sufficient length as to allow of at least two feet for every five such persons employed at any one time, and having a constant supply of warm water from taps or jets above the trough at intervals of not more than two feet; or
(ii.) at least one lavatory basin for every five such persons employed at any one time, fitted with a waste-pipe and plug, and having either a constant supply of hot and cold water or warm water laid on, or (if a constant supply of heated water be not reasonably practicable) a constant supply of cold water laid on, and a supply of hot water always at hand when required for use by such persons;

and for the use of all persons employed in the crystal department or in packing—
(b) sufficient and suitable bath accommodation with hot and cold water laid on and a sufficient supply of soap and towels.

11. A Bath Register shall be kept containing a list of all persons employed in the crystal department and packing, and an entry of the date when each person takes a bath.

Part II.—Duties of Persons Employed.

12. Every person employed in a *chrome process* shall present himself at the appointed time for examination by the *Surgeon*, in pursuance of Regulation 5 (a).

13. No person employed shall, after *suspension*, work in any *chrome process* without written sanction from the *Surgeon*, entered in the Health Register.

14. Every person employed in any *chrome process* shall deposit in the place or places provided in pursuance of Regulation 9 (b) all clothing put off during working hours.

15. Every person for whose use an overall suit is provided in pursuance of Regulation 7 (a) shall wear the overall suit when employed in grinding the raw materials, and, on leaving the premises, deposit it in the place provided under Regulation 9 (c).

16. Every person for whose use a respirator is provided in pursuance of Regulation 8 shall wear the respirator while employed in packing.

17. Every person employed in grinding the raw materials, or in the crystal department, or in packing, shall, before leaving the premises, thoroughly wash the face and hands.

18. Every person employed in the crystal department or in packing shall take a bath at the factory at least once a week; and, having done so, he shall at once sign his name in the Bath Register with the date; provided that
This Regulation shall not apply in the case of a workman who is unwell.

19. No person shall take a meal in the crystal department.

20. No person employed shall interfere in any way, without the concurrence of the occupier or manager, with the means provided for the carrying out of these Regulations.

DESTRUCTION OF ROOTS OF TREES.

To the Editor of the Chemical News.

Sir,—I have acquired about 20 acres of land lately covered with timber (fir). The timber has been sawn off as close to the ground as possible, and the job of getting the roots out is much more laborious and slow than I thought it would be. Could you tell me if there is any chemical, acid, or oil that would consume or rot them quickly in the ground? In the ordinary course of nature I suppose they would rot away in about ten years, but I would like it broken up and under crop much earlier than that.—I am, &c.,

William Malloy.

Reaction of Nitroprussiate with Acetone.—Livio Cambi.—It has long been known that nitroprussiates give a colour reaction with acetone in presence of alkali, but the mechanism of the reaction was unknown. The author has now shown that the coloration is due to the formation of isonitrosoketones. All ketones and aldehydes with the group —CO—CH_n— give the reaction; acetyl acetone, $CH_3.CO.CH_2.CO.CH_3$, gives it very strongly.—*Atti della Reale Accademia dei Lincei*, xxii., No. 6.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Academie des Sciences. Vol. clvi., No. 18, May 5, 1913.

Preparation of Barium.—Camille Matignon.—To prepare metallic barium a mixture is made of 3 parts of BaO to 1 atom of silicon, and it is placed in a steel tube, closed at one end, and heated to 1200° in a porcelain tube in which a vacuum is maintained. The metal distils and condenses on the cooler parts of the steel tube. Without taking any special precautions the author thus obtained a specimen containing 98·5 per cent of barium. Pure amorphous silicon can be used, or a rich ferro-silicon.

Action of Reducing Agents on Chloraloses.—M. Hanriot and A. Kling.—Aluminium amalgam in acid or neutral medium removes 1 atom of chlorine from the molecule of a chloralose. Sodium amalgam in an acid medium gives the same reaction, but it also with difficulty removes a second chlorine atom, while in an alkaline medium the second reaction predominates. Sodium dissolved in liquid ammonia removes 3 atoms of chlorine from chloraloses, the product of the reaction being complex.

Synthesis in the Indigoid Group.—A. Wahl and P. Bagard.—When oxindol condenses with isatin in concentrated sulphuric acid solution, sulphonation occurs and disulphonic isoindigotin acid is obtained. When isatin is replaced by its substituted derivatives disymmetrical substituted isoindigos are obtained. Chloride of isatin reacts with oxindol in a benzene medium to give indirubin, and the substituted isatin chlorides give substituted indirubins, which are violet-coloured dyes.

Preparation of Carbon Tetraiodide. — Marcel Lantenois.—Carbon tetraiodide can be prepared by heating lithium iodide with carbon tetrachloride in a sealed tube *in vacuo* for five days. The temperature must be kept at 90—92°, and after elimination of the excess of the tetrachloride the products of the reaction are taken up with water, and the iodide is separated off, washed, and dried. The yield is 33 per cent. The hydrated iodides of magnesium and zinc can be used for the same purpose, but owing to the readiness with which they are hydrolysed the iodide of carbon is rapidly transformed into iodoform by the hydriodic acid generated. When a very alkaline solution of potassium iodide is heated to 80—90°, a small proportion of acetone is added and then concentrated hypochlorite, tetraiodide of carbon is obtained containing only 10 per cent of iodoform. The tetraiodide can be extracted in a state of great purity by means of petroleum ether and benzine. It crystallises in ruby-coloured octahedra, possessing a very characteristic smell. Its density is 4·5 at 0°. Its best solvents are carbon disulphide, benzine, and acetone.

Vol. clvi., No. 20, May 19, 1913.

Monomethylcamphoroxime.—A. Haller and Edouard Bauer.—When methylcamphoroxime is prepared by means of chlorozincate of hydroxylamine two oximes are formed, one active and the other inactive. The raw oxime gives two phenylurethanes, the first of which is dextrotatory while the other is racemic. The dextro oxime gives rise to a dextro methylcampholenic nitrile, which on hydration yields inactive methylcampholenic amide, and on hydrolysis inactive methylcampholenic acid. Probably methylcampholenic nitrile is analogous to α-campholenic nitrile, and when it is hydrated and hydrolysed it undergoes molecular transposition, its derivatives being β-campholenic compounds.

Variations of Magnetic Rotatory Power in Changes of State.—J. Chaudier.—In the passage from the liquid to the solid state the magnetic rotatory power of active substances is unchanged if the liquid on congelation gives irse to an amorphous substance of vitreous appearance; on the other hand, it entirely disappears if the solid formed has a crystalline structure. The magnetic rotatory power of active substances in the gaseous state, calculated on the assumption that the phenomenon varies as the density, is higher than, or nearly equal to, the rotatory power as directly observed. Thus, while the ordinary rotatory power is preserved in the passage from the liquid to the gaseous state, the magnetic rotatory power generally diminishes, sometimes by one-half, and, moreover, there seems to be a relation between this variation and the magnetic rotatory dispersion of active substances.

System Manganese-silver.—G. Arrivaut.—The author has studied the system manganese-silver thermically, microscopically, and chemically, and has also determined the electromotive forces, using an electrode of silver depolarised with manganese dioxide and immersed in a 10 per cent solution of manganese sulphate. All these methods of investigation show that manganese and silver form a compound $MnAg_2$. This compound gives a continuous series of mixed crystals with silver, and the limit of its miscibility in the liquid state with manganese is at about 30 per cent of manganese.

Quantitative Study of the Absorption of Ultra-violet Rays by Alkaloids of the Atropine Group.—Marcel Gompel and Victor Henri. — The absorption spectrum of atropine shows three bands at $\lambda = 2645$, 2580, and 2505. The constitutional formula of apoatropine differs from that of atropine only in the existence of a double bond, and hence it would be expected that its absorption would be greater, which is found to be actually the case. The absorption spectrum of cocaïne is very different from those of the two preceding alkaloids. It possesses three bands at $\lambda = 2814$, 2722, and 2314, that at 2314 being very well marked.

Benzoyl Cyanhydrines of Ketones and the Amides and Acid Alcohols derived from them.—J. Aloy and Ch. Rabaut.—Good yields of the benzoyl cyanhydrines of ketones can be obtained if one molecule of KCN and one molecule of acetone are thoroughly shaken and one molecule of C_6H_5COCl is added drop by drop. The mixture has to be very thoroughly shaken, the operation taking two or three hours. The cyanhydrines are generally well crystallised stable compounds, which are readily transformed into the corresponding benzoyl amides and into tertiary acid alcohols containing no benzoyl group.

Characterisation of Chlorinated Ketones.—E. E. Blaise.—In order to identify the chlorinated ketones it is most convenient to prepare the normal semicarbazones, which possess conveniently low fusion points. Nearly all chlorinated ketones are rapidly converted into semicarbazones by the action of 1 to 1·5 mol. of hydrochloride of semicarbazide dissolved in water.

MISCELLANEOUS.

Action of Alkaline Sulphites on Ethylenic Acids.—J. Bougault and M. Mouchel-la-Fosse.—Many acyclic and cyclic ethylenic acids combine with sodium bisulphite to give the sodium salts of sulphonic acids by fixation of the bisulphite at the double bond. The fixation occurs more easily and rapidly the more electronegative groups the ethylenic acid contains. The sulphonic acids obtained are very soluble in water, even when they are derived from insoluble acids. By means of this reaction it is possible to determine approximately the amount of ethylenic acid present in a mixture with saturated acids, and to separate the saturated acids in a state of purity.—*Journal de Pharmacie et de Chimie*, vol. vii., No. 10.

ERRATUM.—P. 16, col. 1, line 22, *read* "*Zeit. Anorg. Chem.*, 1913 Bd. 82, p. 249."

THE CHEMICAL NEWS.

Vol. CVIII., No. 2800.

THE WALDEN REACTION.

By CECIL L. HORTON.

This reaction seems to affect only the α- and β-amino-halogen and hydroxy acids. These acids, however, may be either secondary or tertiary. The changes may be represented by

$$NH \rightleftharpoons OH \rightleftharpoons Cl$$
$$\xrightarrow{\hspace{3em}}$$
$$\xleftarrow{\hspace{3em}}$$

The reagents employed are NOBr, NOCl, NH_3, PCl_5, $SOCl_2$, Ag_2O, KOH, HNO_2, KNO_2 and HCl, MeOH, and H_2O.

In only one case does the reagent exhibit a constant behaviour, that is in the case of PCl_5. In all other cases the sign of the active product is sometimes the same as and sometimes the opposite to that of the parent body. There seems to be no experimental evidence as to whether thionyl chloride is constant in its behaviour or whether it resembles the other reagents.

Disregarding the exception named above, it would seem that the direction of the reaction is dependent on the number of free carboxyls. For an even number of free carboxyls the influence on the sign of the active body is the reverse of that if the number of free carboxyls be odd.

Reagent.	Reaction.		No. of free carboxyls.
Ag_2O	*l*-α-Bromopionic acid	*d*-Lactic acid	1
	l-Phenylchloracetic acid	*d*-Mandelic acid	1
	l-Chlorsuccinic acid	*l*-Malic acid	2
	l-α-chlor-α-phenyl propionic acid	*d*-α-Hydroxy acid	1
KOH	*d*-Chlorpropionic	*d*-Lactic acid	1
NaOH	*d*-Clorsuccinic	*l*-Malic acid	2
	d-Phenylchloracetic acid	*d*-Mandelic acid	1
	(In general, the reverse	of silver oxide).	
MeONa	*d*-Phenylchloracetic acid	*d*-Methoxy acid	1
PCl_5	Always constant.	Change *l*-d	
$SOCl_2$	*l*-α-Hydroxy-α-phenyl-propionic acid	*l*-Chlor acid	1
	d-β-Hydroxy-β-phenyl-propionic acid	*d*-β-Chlor acid	1
H_2O	*l*-β-Chlorbutyric acid	*d*-β-Hydroxy acid	1
	l-β-Chlorphenylpropionic acid	*d*-β-Hydroxy acid	1
HNO_2	*d*-β-Aminobutyric acid	*l*-β-Hydroxy-butyric acid	1
	l-Asparine	*l*-Malic acid	2
	l-Aspartic acid	*l*-Malic acid	2
	l-Asparine probably passes through *l*-aspartic acid		
NOCl	*l*-Asparine	*l*-Chlorsuccinic acid	2
	l-Aspartic acid	*l*-Chlorsuccinic acid	2
NOBr	*d*-Alanine ester	*d*-α-bromopropionic ester	0
	d-Alanine	*l*-α-Bromopropionic acid	1
	l Aspartic ester (mono)	*d*-Bromosuccinic ester (mono)	1
	l Aspartic acid	*l*-Bromosuccinic acid	2
	l-Valine	*d*-α-Bromoiso valeric acid	1
NH_3	*l*-α-Bromopropionic acid	*l*-Alanine	1
	d-α-Bromoisovaleric acid	*l*-Valine	1(*a*)
	d-α-Bromoisovaleryl glycerine	*d*-Valine (on hydrolysis)	1

(*a*) The exception named above.

Omitting the constant reagent, the following table shows the effect on acids with one free carboxyl:—

Reagent.	Direction of reaction.
$SOCl_2$	*d*—*d*
Ag_2O	*d*—*l*
KOH, NaOH, $NaOCH_3$	*d*—*d*
NOBr, NOCl	*d*—*l*
H_2O	*d*—*l*
NH_3	*d*—*d*
HNO_2	*d*—*l*

Thus NOBr on *d*-alanine ester (no free carboxyl) gives rise to *d*-α-bromopropionic ester. On the other hand, the same reagent on *d*-alanine itself (one free carboxyl) gives rise to *l*-α-bromopropionic acid.

From the twenty-six examples given above there seems to be only one exception, that of *d*-α-bromoisovaleric acid, which under the influence of ammonia gives rise to *l*-valine when the *d*-isomer would be expected. It is thus possible to predict the sign of any product under the influence of any definite reagent by studying the number of free carboxyl groups present.

The behaviour of the dialkyl esters of dibasic acids and of the mono- di-, and tri-alkyl esters of the tri-basic acids, &c., would be of interest.

THE ABSORPTION OF LIGHT BY WATER CHANGED BY THE PRESENCE OF STRONGLY HYDRATED SALTS, AS SHOWN BY THE RADIOMICROMETER.*

New Evidence for the Solvate Theory of Solution.

By J. SAM GUY, E. J. SHAEFFER, and HARRY C. JONES.

(Concluded from p. 30).

When salts which are strongly hydrated in aqueous solutions are not very concentrated, the difference between the transparency of the salt solution and that of water of the same depth of layer as the water in the solution is not so pronounced. This is what would be expected, since the total amount of water combined with the dissolved salt increases with the concentration of the solution. The data given in Table V. bring out this fact.

The depth of layer of the different solutions for which the results are recorded in Table V. was the difference between 21 and 1 mm., *i.e.*, 20 mm. The results are, therefore, comparable with those recorded in Table III., the difference being a difference in the concentrations of the solutions used. It will be seen from a glance at the table that the difference between the transmission of the solution and that of water at the same depth as the water in the solution is very much less for the more dilute than for the more concentrated solutions. As has already been pointed out, this is exactly what would be expected in terms of the solvate theory applied to the phenomenon in in question.

Considerable work was done in *comparing directly* the transmission of a solution and that of water having the same depth as the water in the solution in question. The deflection of the radiomicrometer as given by the solution is in the column marked "I sol." and the deflection as given by water having the same depth as water in the solution is given in the column marked "I_0 H_2O."

* From the *American Chemical Journal*, xlix., No. 4.

TABLE V.

λ.	2·69/N $CaCl_2$. I/I₀.	H_2O.	2·48/N $MgCl_2$. I/I₀.	H_2O.	0·308/N $Al_2(SO_4)_3$. I/I₀.	H_2O.
710	96	94	95	95	97	96
724	95	96	93	96	98	96
741	95	95	90	95	95	93
760	94	96	92	95	95	95
776	93	97	93	95	95	95
798	90	98	91	95	96	96
818	93	97	91	93	95	96
836	91	96	89	93	93	95
855	91	92	88	92	92	92
878	90	92	84	90	90	91
900	88	90	84	88	89	86
922	89	92	81	86	82	85
947	82	86	78	83	78	80
958	75	79	72	76	73	75
964	70	74	70	73	68	69
969	65	69	62	64	62	62
974	58	61	58	58	57	54
979	50	52	50	51	50	46
982	44	47	46	46	46	42
985	40	43	42	43	43	40
991	39	41	40	41	41	39
1007	38	40	41	42	40	40
1013	39	42	40	44	40	40
1019	40	43	40	44	41	41
1025	43	45	44	41	43	43
1032	45	47	47	44	45	46
1037	48	50	50	46	47	48
1042	51	52	52	48	49	49
1046	56	56	56	54	53	54
1059	61	59	58	55	60	59
1065	65	64	64	62	59	62
1072	69	67	67	64	63	65
1078	70	69	69	67	65	69
1085	72	72	72	68	68	72
1100	73	73	73	71	69	73
1113	72	74	74	72	68	74
1138	72	74	74	70	67	72
1148	66	69	69	67	64	67
1158	67	62	62	60	58	62
1165	57	58	58	58	54	54
1172	52	51	53	52	47	46
1179	46	39	42	42	39	35
1186	30	27	31	27	28	25
1193	20	19	21	20	20	16
1200	13	14	15	15	14	12
1206	12	11	12	13	12	10
1213	11	11	12	12	11	10
1220	11	10	11	11	11	10
1227	10	9	10	10	10	9

TABLE VI.

λ.	I sol./$Al_2(SO_4)_3$.	I₀/H_2O.	I sol./KCl.	I₀/H_2O.
710	50	51	53	53
724	58	58	56	56
741	62	63	67	68
760	72	72	77	77
776	75	76	88	90
798	83	83	98	99
818	82	82	108	109
836	93	94	116	116
855	97	97	124	124
878	105	105	129	130
900	105	105	140	138
922	112	112	140	140
947	113	113	142	142
958	109	106	136	136
964	107	100	129	125
969	104	93	118	116
974	98	83	108	106
979	93	73	92	92
982	82	66	83	83
985	80	64	78	80
991	78	62	78	80
1007	78	65	78	81
1013	74	65	81	85
1019	77	68	84	88
1025	80	75	96	96
1032	84	77	100	101
1037	91	84	112	108
1042	92	92	119	116
1046	99	99	125	120
1059	105	105	141	136
1065	109	112	150	145
1072	114	119	159	153
1078	118	125	164	158
1085	122	132	168	164
1100	128	140	176	172
1113	129	142	178	175
1138	127	142	174	170
1148	123	131	164	162
1158	112	118	161	159
1165	108	111	157	154
1172	99	94	132	126
1179	87	74	107	100
1186	68	49	73	66
1193	54	35	50	48
1200	42	26	24	36
1206	35	23	39	32
1213	30	21	25	30
1220	28	20	24	29
1227	26	19	24	28
1241	24	19	23	26
1255	23	18	25	27

The results obtained for aluminium sulphate having a concentration 1·02/N and for 4/N potassium chloride are given in Table VI. The depth of solution used was 20 mm. and the depth of water that of the water in the solutions in question.

In this work duplicate measurements were made with the radiomicrometer for nearly every solution of all the substances worked with at the various wave-lengths studied. It was found that the readings for the different solutions of the same substance having the same concentration were, for a given wave-length, different from one another to the extent of somewhat less than 2 per cent. From this it seems fair to assume that the error in our work was not greater than 2 per cent.

An examination of the tables of data for potassium chloride, ammonium chloride, and ammonium nitrate, that is, for those substances which, in aqueous solutions, combine with very little water, as was demonstrated by the freezing-point method, shows that for all wave-lengths studied the solution and water of the same depth as the water in the solution have practically the same transmission. The dissolved substance does not combine with the solvent water, and the water in the solution has almost exactly the same effect upon light as so much pure water would have. This is exactly what would be expected from our knowledge of the absorption of light by dissolved substances and by the solvent. When we began this work we supposed that the water in the solution, whether it was combined with the dissolved substance or not, would have the same power to absorb light as so much pure solvent water. We shall now see that such is not the case.

The results for the above-named substances were not plotted in the form of curves, since the curve for water and for the solution would practically coincide with one another, the dissolved substance having very little absorption over the region of wave-lengths studied in this investigation.

When we turn to the data in Tables III. and IV. very different relations manifest themselves. These are the data for calcium chloride, magnesium chloride, and aluminium sulphate, that is, for salts which, in aqueous solution, are strongly hydrated, as was shown by the earlier work in this laboratory (Carnegie Institution of Washington, *Publication* No. 60). The solution in these

cases is often more transparent than the same amount of water that is contained in the solution.

That these relations may appear the more clearly, the results obtained for the above-named salts are plotted as curves in Figs. I. to VI. Fig. I. is the curve for calcium chloride having a depth of 20 mm. This was obtained by dividing the deflection produced by 21 mm. of the solution by that produced by 1 mm. of the solution. On the same sheet we have the curve for water having a depth equal to that of the water in the calcium chloride. This curve for water was also obtained by the "differential" method, *i.e.*, by dividing the deflections produced by the deeper solution by those obtained with the more shallow solution, the difference in the depths of water in the two cases being just equal to the depth of water in 20 mm. of the solution in question. Fig. II. is the curve for calcium chloride with a depth of layer of 10 mm. (11—1). The data from which the curve was plotted are contained in Table IV. The smaller depth of solution was used so that the water band between 1·2 μ and 1·3 μ would come out more distinctly. The results for this solution, like those for all the others, are compared with the absorption of a depth of water equal to that of the water in the solution. The absorption of the water in this, as in all other cases, was obtained by the "differential" method.

Fig. III. is the curve for magnesium chloride having a depth of 21 − 1 = 20 mm. and the corresponding water curve. The data from which these curves are plotted are given in Table III.

Fig. IV. is the curve for magnesium chloride having a depth of 1 cm., also obtained by the "differential" method. These data are taken from Table IV.

Fig. V. is the curve for aluminium sulphate having a depth of 20 − 1 = 20 mm. and the corresponding absorption curve for water.

Fig. VI. is the curve for aluminium sulphate having a depth of 11 − 1 = 10 mm. and the corresponding water curve.

Fig. I. shows the relative absorption of water and of the solution of calcium chloride having a concentration of 5·3 normal and a depth of 20 mm. The corresponding water curve is marked throughout by the symbol "H_2O." The solution is the more transparent from 0·9 μ to nearly 1 μ. The water then becomes the more transparent over a short region of wave-lengths. From 1·05 μ to 1·2 μ the solution is the more transparent. In this region the solution becomes as much as 25 per cent more transparent than the pure water, as can be seen by comparing the points on the "water" curve with the corresponding points on the curve for the solutions which are vertically above the points on the water curve. The water becomes appreciably more transparent only at and near the bottom of the "water band" having a wave-length of approximately 1 μ. This is the effect that we would expect to get if the dissolved substance exerted a "damping" effect on the absorption of light by water.

It will be recalled that the salts which do not form hydrates show, in aqueous solution, practically the same absorption as the corresponding amount of water. It would, therefore, seem reasonable to account for the differences in the case of non-hydrating and strongly hydrating salts as due to the water of hydration, or the water that, in this case, is combined with the calcium chloride.

The curves in Fig. II. are for a smaller depth of the same solution of calcium chloride. This figure brings out

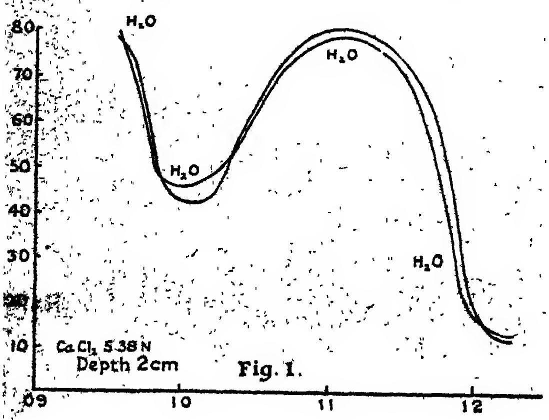


Fig. I.

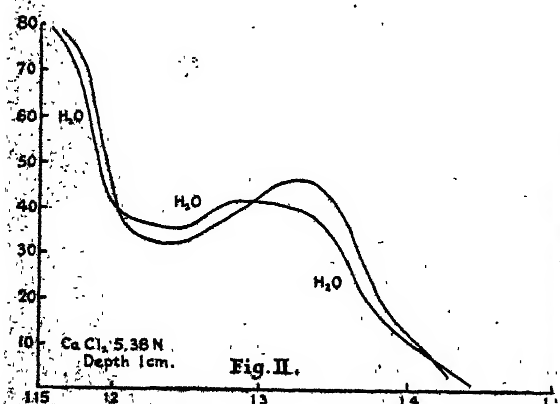


Fig. II.

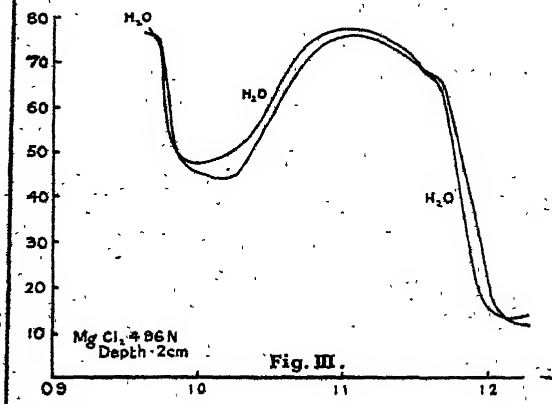


Fig. III.

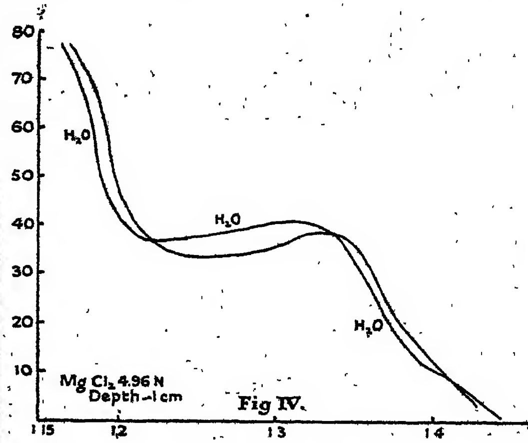


Fig. IV.

the same general relations as was shown in Fig. I. The water curve in the region 1·25 μ is above that of the solution, showing that water in this region for the more shallow depth of solution is more transparent than the solution. The additional feature brought out by this figure is the water band in the region 1·4 to 1·5 μ. After the first-named water band is passed the solution becomes more transparent than the water, and remains so until the wave-length 1·42 μ is reached. Here both the solution and the water are practically opaque, as is shown by both the curves approaching the abscissæ.

The curve for magnesium chloride having a depth of 20 mm. is almost exactly a duplicate of that for calcium chloride having the same depth. Practically the only difference worthy of mention is in the region from 1·0 μ to 1·1 μ. In the case of magnesium chloride the water

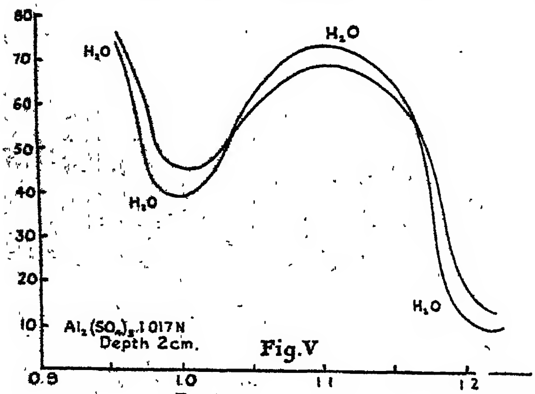


Fig. V.

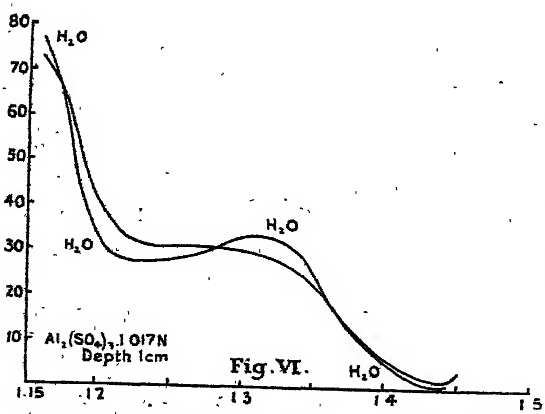


Fig. VI.

remains the more transparent over this region of wave-lengths. In the case of calcium chloride the solution is the more transparent over this region. The difference in the transparency of the water and the solution throughout the region is, however, not very great. From 1·1 μ towards the longer wave-lengths, as we come down the descending arm of the curve towards the second water band, the water in the case of the magnesium chloride, as in the case of calcium chloride, becomes much more transparent than the solution, the differences here being of the same order of magnitude as those with calcium chloride.

Fig. IV. gives the results for magnesium chloride with a depth of layer of 1 cm. The same relations hold in Fig. IV. as in Fig. III., for the relative transparency of the water and of the solution. The water becomes the more transparent from 1·22 μ to 1·34 μ. For the longer wave-lengths the solution becomes more transparent until the region 1·41 μ is passed. For wave-lengths longer than 1·41 μ the transmission of both solution and water is practically zero, that is, they both become opaque to the longer wave-lengths.

The results in Fig. V. bring out some new features of interest and importance. These are the results that were obtained with aluminium sulphate. The new feature shown by the curve for aluminium sulphate, as compared with those for calcium chloride and magnesium chloride, is that at the minimum of the curve corresponding to wave-length 1 μ the solution is more transparent than the corresponding water. Beyond the wave-length 1·04 μ the water becomes the more transparent with aluminium sulphate as with magnesium chloride. Beyond the wave-length 1·6 μ the solution becomes more transparent in this case as with magnesium chloride and calcium chloride.

If we turn to Fig. VI. the relations are as follows:—In the region of 1·2 μ the water is more opaque. From 1·209 μ to 1·306 μ the water becomes the more transparent. From 1·306 μ to the longest wave-length studied, the solution again becomes more transparent than the corresponding layer of water.

An examination of all the results thus far obtained bearing on this problem leads us to conclude that the greater transparency of the solution as compared with the water in the solution must be due to some action of the dissolved substance on the solvent water. The question remains, what is this action?

We have seen from our earlier work on the absorption spectra of solutions, which has been in progress in this laboratory continuously for the past eight years, that the solvent can have a marked effect on the power of the dissolved substance to absorb light. This was first shown by Jones and Anderson (Carnegie Institution of Washington, Publication No. 110), and a large number of examples of this effect have since been found by Jones and Strong (*Ibid.*, Nos. 130 and 160). We interpreted the effect of the solvent on the power of the dissolved substance to absorb light as due to a combination between a part of the liquid present and the dissolved substance. This enabled us to explain a large number of facts that were brought to light for the first time by the investigations of the absorption spectra of solutions which have been carried on in this laboratory. Many of the phenomena which were thus explained, it seemed, could not be explained in terms of any other suggestion that has thus far been made. In a word, the solvate theory of solution, as proposed by Jones about a dozen years ago (*Am. Chem. Journ.*, 1900, xxiii., 89) to supplement the theory of electrolytic dissociation in order that we might have a theory of the real solutions which we use in the laboratory, and not simply a theory of ideal solutions as the theory of electrolytic dissociation alone must be regarded, has served good purpose in explaining the phenomena that have been previously observed in connection with the absorption of light by solutions of dissolved substances.

We are inclined to explain the phenomena recorded in this paper by means of the same theory. For solutions of those substances which have been shown by entirely different methods not to hydrate to any appreciable extent, the absorption of light by the solution and by a layer of water equal in depth to that of the water in the solution is, to within almost the limit of experimental error, the same.

For those substances which have been shown to form complex hydrates, however, the absorption of light by their solutions and by a layer of water equal in depth to that of the water in the solution is very different. The water in these solutions is usually more opaque to light than the solution, or, what is the same thing in other words, a solution is more transparent than the water that is present in the solution.

The most rational explanation of this phenomenon appears to us to be that the part of the water that is combined with the dissolved substance has a smaller power to absorb light than pure, free, uncombined water. The

fact that we are able to detect the difference between the water in the solution and pure water, by its action on light, we regard as good evidence in favour of the water in the solution being different from pure, free water. This difference, it seems to us, can be readily accounted for by the fact that a part of the water present in the solution is in combination with the dissolved substance.

We have carried out similar investigations with aluminium nitrate, but the concentration of the strongest solution that could be obtained was not sufficiently great to show the phenomenon in question. We, therefore, do not incorporate the results obtained with this substance. That the solutions must be very concentrated to show clearly the phenomenon with which we are dealing is shown by the results given in Table V. Here the solutions of the three salts in question that were used are more dilute than those for which the results are tabulated in Tables III. and IV. An examination of this table will show that the phenomenon in question does not manifest itself to anything like the same extent as with the more concentrated solutions. This is exactly what we would expect in terms of the solvate theory of solutions. The more concentrated the solution the larger the total amount of the water present combined with the dissolved substance. If combination between water and the dissolved substance explains the facts recorded in this paper, then the larger the amount of water present that is combined with the dissolved substance, the more pronounced the phenomenon in question.

The results obtained with aluminium sulphate bring out the same facts shown by calcium chloride and magnesium chloride. They, however, show in addition that water is more transparent in the region of $1 \cdot 1\ \mu$ and more opaque at $1\ \mu$. That the sulphate should not agree throughout with the chlorides is really not surprising, since the sulphates show abnormal results in almost every particular. This is probably due, in part at least, to the large amount of polymerisation which the sulphate molecules in general undergo in the presence of even water as a solvent. It should also be remembered in the present connection that, while calcium chloride and magnesium chloride crystallise with only six molecules of water, and are, therefore, only largely hydrated, aluminium sulphate crystallises with 18 molecules of water, and is, therefore, very largely hydrated.

The results in Table VI. are, as has already been stated, the radiomicrometer deflections for a solution of aluminium sulphate and those for water having the same depth as the water in the solution in question, and the corresponding data for potassium chloride. A comparison of the two columns for potassium chloride and its corresponding water shows that the two are almost equally transparent to all the wave-lengths studied.

A comparison of aluminium sulphate with its corresponding water brings out the phenomenon that we are now discussing in a very pronounced manner. It is for this reason that the data in this paper are given.

One other relation of a general character should be pointed out. The curves upon all six of the figures show that the addition of salt to water shifts the absorption towards the longer wave-lengths. This is analogous to what has already been found by Jones and Uhler (Carnegie Institution of Washington, Publication No. 60), Jones and Anderson (*Ibid.*, Publication No. 110), Jones and Strong (*Ibid.*, Publications No. 130 and No. 160), and Guy and Jones (*Am. Chem. Journ.*, 1913, xlix., 1), when the absorption of salts as affected by the water present was studied. It was found that rise in temperature and increase in the concentration of the solution both tended to shift the absorption of the salt towards the longer wave-lengths. The effect of rise in temperature and the increase in the concentration of the solution tended to simplify the hydrates in combination with the particles of the salt. The resonator within this simplified system seems to vibrate so as to shift the absorption bands towards the red.

The effect of the salt on the absorption of the water is the same as that of rise of temperature and increase of concentration on the absorption of the dissolved substance. We should naturally look for a similar explanation of the two sets of phenomena. It has been suggested by Dr. Guy that the effect of the salt on the absorption of light by water may be due to the breaking down of the associated molecules of water by the dissolved substance. This would be in keeping with the discovery made by Jones and Murray (*Am. Chem. Journ.*, 1903, xxx., 193), that one associated substance when dissolved in another associated substance diminishes its association.

In terms of this explanation, however, it is a little difficult to see why non-hydrated salts, such as were used in this work, do not also diminish the association of water and cause a shifting of its absorption bands towards the longer wave-lengths. It may be that the effect of the dissolved substance in breaking down the association of the water is pronounced only in the case of water of hydration or the water that is combined with the dissolved substance, and that the explanation offered above is fundamentally correct.

In conclusion we wish to express our thanks to Professor A. H. Pfund, who has made many valuable suggestions during the progress of this work. We would also express our thanks to Dr. E. P. Wightman, who has kindly drawn the curves for us.

ALLOYS OF COBALT WITH CHROMIUM AND OTHER METALS.*

By ELWOOD HAYNES.

As in organic nature, certain animal and vegetable forms have undergone modifications, and thus, as it were, fitted themselves to live in a new environment, so it has been found possible in certain instances to form new metallic combinations which are practically immune to the natural conditions that exist on the earth at the present time. A few of the rare metals, such as gold, silver, and the metals of the platinum group, are found native, but the commoner heavy metals are nearly always found in the form of oxides or sulphides.

For a number of years I have made experiments with a view to finding certain metallic combinations of alloys which would not only resist oxidation and other harmful influences, but would also possess valuable physical properties, which would render them fit for special services. The first decisive step made in this direction was the discovery of an alloy of nickel and chromium in 1898. The properties of this alloy have already been described in a previous paper (*Journ. of Indus. and Eng. Chem.*, ii., 397). Immediately following the discovery of the nickel-chromium alloy, I produced an alloy of cobalt and chromium. This has likewise been described in the previous paper, but the range of proportion between the cobalt and chromium is so great, and the combination is modified to such a marked degree by the introduction of other substances, that I have felt justified in reading another paper on this subject, describing more fully my researches in this particular direction.

As early as 1907 and 1908, I made alloys or combinations of cobalt, chromium, and tungsten; cobalt, chromium, and molybdenum; and cobalt, chromium, tungsten, and molybdenum. I have made alloys of cobalt and chromium containing zirconium, tantalum, thorium, titanium, vanadium, &c. I have also added to the cobalt-chromium alloys the non-metallic elements, carbon, silicon, and boron. Some exceedingly interesting results have been obtained from these various combinations, and while further investigation is necessary in order to fully

* Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912. From the *Journal of Industrial and Engineering Chemistry*, v., No. 3.

determine their chemical and physical properties, a number of them have shown interesting economic possibilities.

The preliminary fusions were made in graphite crucibles by means of a furnace operated by natural gas. I was later obliged to use crucibles of a special composition, not only to avoid the contamination of the metal by carbon from the crucible, but also because they proved more reliable under long-continued heating than those made of graphite.

The metal tungsten alloys readily with chromium and cobalt in all proportions. When added in small quantity to the cobalt-chromium alloy, it seems to have little influence on the properties of the combinations, but if the proportion rises to 2 per cent or 3 per cent, a notable effect is produced. Generally speaking, the cobalt-chromium alloy becomes harder and more elastic, especially if it contains a small amount of carbon, boron, or silicon.

The following experiment shows the effect of melting the alloy in a graphite crucible:—90 grms. of cobalt, 6·3 grms. of tungsten, 18 grms. of chromium, together with a small quantity of calcium silicide, were introduced into a graphite crucible. The resulting alloy was very hard, and the crucible much eroded on the inside. The bar could be slightly flattened at one end, and after being made into a cold chisel, showed remarkable qualities. It would not only scratch glass, but also quartz crystal. It was quite tough at ordinary temperatures, and would cut small chips or shavings from a piece of stellite. At a bright yellow heat it showed signs of fusion, and became covered with a skin of oxide.

An alloy was made by melting the following in a special crucible:—Cobalt rondelles 80 grms., chromium 20 grms., tungsten 7 grms., calcium silicide 10 grms., calcium carbide 5 grms. As soon as the above were melted, the crucible cover was removed, and 15 grms. of an alloy of cobalt and boron were introduced. The crucible lid was then replaced and the heating continued. A heavy, thick slag formed, which was removed before pouring the metal. The resulting bar was very hard and *elastic*, but drew only slightly under the hammer, and then broke. A cold chisel made from the cast metal cut iron readily. The bar was broken up and remelted with about one-third of its weight of an alloy of cobalt, chromium, tungsten, and carbon. The result was a fine-grained alloy which was very *elastic*, and would draw out to a considerable degree under the hammer without checking. Its elastic limit must have been very high, since when it broke, the pieces were thrown violently.

Taking the alloy of chromium and cobalt as a basis, and holding the proportion of chromium at 15 per cent of the entire mixture, it was found that the alloy gradually increased in hardness with the percentage of tungsten. When the quantity of tungsten rises to 5 per cent, the alloy becomes distinctly harder, particularly when forged under the hammer. When the tungsten reaches 10 per cent, the metal still forges readily, and a tool formed from the alloy takes a fine cutting edge. This alloy is suitable for both cold chisels and wood-working tools. When the tungsten rises to 15 per cent, the metal can still be forged, but great care is necessary in order to avoid checking. The alloy is considerably harder than that containing 10 per cent of tungsten and is excellent for cold chisels. When the tungsten rises to 20 per cent, the alloy is still harder, and can be forged to a small extent. It makes good lathe tools for cutting steel and other metals at moderate speeds. When the tungsten rises to 25 per cent, a very hard alloy results, which cannot be forged to any extent, but casts readily into bars which may be ground to a suitable form for lathe tools. These tools have shown great capabilities, particularly for the turning of steel, since they are very strong, and retain their hardness at speeds which almost instantly destroy the cutting edge of a steel tool. The tungsten may be still further increased to 40 per cent, and the alloy will retain its cutting qualities, and for turning cast iron this alloy answers even better than that containing 25 per cent. When the tungsten reaches 40 per cent or more, the alloy becomes so hard that it will not only scratch glass, but will readily scratch quartz crystal. A small drill, made of this material, drilled a hole through the wall of a glass bottle without the addition of any liquid or other lubricant. A three-eighth inch square cast bar, when ground to a suitable edge, was set in a tool-holder attached to a lathe. The workman who had operated the lathe had been able to turn to form 26 cast iron wheels in 10 hours with a steel tool of the same size. The stellite tool turned 49 of these wheels to form in the same time. The steel tool was ground 50 times during the operation, while the edge of the stellite tool was dressed slightly by a carborundum whetstone, after its day's work was completed. A set of steel cutters, placed in the boring head of a cylinder-boring machine, were able to bore from 26 to 28 holes in ten hours. These cutters were replaced by others made of stellite, which performed the work in three hours and twenty minutes, or a little more than one-third the time. Not only was the speed of the mill doubled, but the feed also, and notwithstanding this severe ordeal, the stellite cutters were only slightly worn, while it would have been necessary to re-grind the steel cutters at least two or three times for the same service at slower speed. Some remarkable results were obtained in the turning of steel on the lathe. For example, a cylindrical bar of annealed nickel-chrome steel, about 2½ inches in diameter, was placed in a lathe and turned with a steel tool at about as high a speed as the steel would permit without "burning." The steel tool was then replaced by one of stellite, and the speed at the same time increased to two and two-thirds its former speed. The stellite tool retained its edge under these severe conditions, and produced a shaving weighing one and two-tenths pounds in one-half minute. Just what the effect of the alloy will be in machine shop practice is at present somewhat difficult to determine. In my opinion, however, it will not fully supersede high-speed steel in the machine shop, but in cases where rapid work is the main consideration it will doubtless replace high-speed steel.

When molybdenum is added to a 15 per cent cobalt-chromium alloy, the alloy rapidly hardens as the molybdenum content increases, until the content of the latter metal reaches 40 per cent., when the alloy becomes exceedingly hard and brittle. It cuts keenly and deeply into glass, and scratches quartz crystal with ease. It takes a magnificent polish, which it retains under all conditions, and on account of its extreme hardness its surface is not readily scratched. When 25 per cent molybdenum is added to a 15 per cent chromium alloy, a fine-grained metal results, which scratches glass rather readily, and takes a strong keen edge. Its colour and lustre are magnificent, and it will doubtless find a wide application for fine hard cutlery. It cannot be forged, but casts readily, and its melting-point is not abnormally high.

If carbon, boron, or silicon be added to any of the above alloys, they are rendered much harder, though their effect is not always desirable, since they tend to render the alloys more brittle.

If either tungsten or molybdenum is added to a cobalt-chromium alloy containing 25 per cent of the latter metal, the hardness of the alloy is rapidly increased. When the percentage of tungsten, for example, reaches 5 per cent, the alloy can be readily forged, and forms an excellent combination for wood-cutting tools, such as chisels, pocket knives, &c. When molybdenum is added to the same mixture of chromium and cobalt, much the same effect is produced, though, generally speaking, a smaller quantity of molybdenum is required to produce a given increase in hardness. In some instances I have found it advisable to add both molybdenum and tungsten to the cobalt-chromium alloys. Generally, the colour and lustre of these alloys, after polishing, are magnificent, and they seem to resist atmospheric influences equally as well as the binary alloy of cobalt and chromium.

NOTES ON THE CHEMISTRY OF PAPER-MAKING.

By THOMAS J. KEENAN, F.C.S.

In an address before the King's County Pharmaceutical Society in the Brooklyn College of Pharmacy on January 14, 1913, the managing editor of *Paper* described some of the operations involved in the manufacture of woodpulp and paper, contrasting them with the work of the pharmaceutical chemist. He demonstrated among other things that the same uncertainty which formerly prevailed in pharmaceutical work—and which still exists to some extent—regarding the extractive or alkaloïdal strength of the ultimate tincture or extract, is experienced by the papermaker in regard to the nature of the product he may obtain after extracting his wood and mixing the residuum with varying proportions of other materials, such as clay, alum, and rosin, in a beater—the modern analogue of the stamping machine or crude mortar and pestle of the mediæval craftsman.

The application of chemistry to papermaking began with the process of treating wood with caustic alkalis or alkaline earths so as to extract a product to replace the pulp made from rags. It had not been overlooked, of course, that the use of chlorine bleach came first, following the discovery of chlorine by Scheele in 1774.

The timber, from which the pulp or cellulose destined to form the finished sheet of paper is produced, varies in quality according to cultivation, soil, and climatic influences in much the same way as do the drug-producing plants, and the quality and quantity of pulp varies according to the class of woods used and the nature of the process, so that uniformity of product is nearly as difficult in the one case as in the other.

The production of a finished paper of uniform and unvarying quality and characteristics, as determined by chemical and microscopical tests, is impracticable, owing to conditions inherent in the process of manufacture. The papermaker cannot tell to a nicety what proportion of the materials which go to make up his "furnish" or formula will be retained in the ultimate paper and what will go out with the water which is drained away from the pulp as it travels on the running wire of the paper machine to the press and drying rolls. In this respect the art of papermaking has not kept pace with the progress of other arts and crafts, though in the direction of mechanical improvements there are few industries in which mechanical invention has been so highly developed or in which engineering as a science plays a more important part, some of the special machinery in the equipment of a modern paper mill being examples of engineering skill that are little short of marvellous in the ingenuity of their construction and operation.

In the primary processes of separating the pulp or cellulose from the wood the pharmacist will see no analogy with any operation known to his art. On the contrary, he will observe methods employed and results obtained as astounding by their destructive wastefulness as by total opposition to galenical methods in the extraction of valuable plant constituents. It is in the intermediate and later stages of papermaking—in the combining of the "furnish," as the assembled ingredients of the formula for a given paper are conveniently termed, and in the testing of papers—that he will note familiar combinations and reactions.

The simplest form of woodpulp, that known as "ground wood," which forms the body of newsprint paper, is produced by pressing logs of cone-bearing trees, such as spruce, balsam, pine, and fir, freed from bark, and cut into short pieces about two feet long, against revolving grindstones, under a stream of water, so that the disintegrated pulpy fibres, torn away from the log, obliquely or against the grain, can be run off into tanks and thence flowed away to undergo a screening and straining operation for the removal of refuse and unground lumps. As the pulp obtained in this way contains the sap, lignin, and resin of the raw wood, substances that are prone to rapid oxidation and discoloration, paper made from it soon deteriorates, becoming brown and brittle, and it is a very perishable product. Pulp of this kind, however, is only used as an admixture with chemically prepared pulp in the manufacture of newsprint and the cheaper grades of book paper, or alone in the manufacture of boards; ground poplar wood being also used to some extent for this purpose.

It is the pulp produced by chemical means which has most interest for the pharmacist, the systems in use being, as already indicated, so much at variance with pharmaceutical work and especially the extractive processes employed in pharmacy. The chief processes are known as the sulphite, the soda, and the sulphate. By the solvent action of the chemical solutions upon the non-fibrous constituents of the wood the cellulose is set free from its enveloping bodies and is recovered to the extent of nearly 50 per cent of the total weight of the wood. The material which is extracted, consisting of all the soluble constituents of the wood—the gums, resins, tannins, and other valuable plant principles which encrust the cellulose—represents to the papermaker so much offal or waste, and, in the soda process, is destroyed by burning, the soda being recovered; and, in the sulphite process, washed into rivers and streams, with a total loss of organic extractives and chemicals.

It is scarcely necessary to emphasise more particularly the sharpness of the contrast that is here presented to the work of the pharmacist, where the end aimed at is the separation of the active and soluble constituents of the plants from the inert insoluble portion; the residue or marc, consisting of broken down weedy tissue and fibres, being rejected. But to illustrate better the contrast in work, a brief description of the sulphite process of pulp-making may be given. The wood, having been cleaned and cut up into pieces from two to five feet in length, as in the ground wood process, is chipped up into small pieces or chips about one-fourth inch to one-half inch thick and boiled under pressure in large steel digesters capable of holding twenty tons of wood at one operation and yielding ten tons of finished pulp. The digesters are lined with heavy cement backing faced with brick, pointed with litharge and glycerin, to prevent contact with the metal.

The sulphite liquor in which the wood is boiled is made by passing sulphur dioxide—obtained by burning sulphur, or iron pyrite, in special ovens—into tanks filled with water and a known quantity of slaked lime (prepared from dolomite). This results in the formation of a solution of the acid sulphites of calcium and magnesium, which is the active solvent agent. The chemistry of the reaction between the wood and the sulphite liquor prepared from dolomite or magnesian limestone is tersely but sufficiently stated by Thorp ("Outlines of Industrial Chemistry," Macmillan, 1911), who explains that the acid sulphites react much like sulphurous acid, but the sulphites combine with the aldehydes formed in the first stages of the decomposition, producing stable and soluble double salts. The organic acids which are also formed decompose the bisulphites and form soluble calcium and magnesium salts, while the sulphurous acid gas is set free, causing a constant increase of pressure within the digester. The acid sulphites also tend to bleach the colouring matter of the fibres by forming colourless compounds with them, but this is a very unstable bleach and the original colour soon returns when the pulp is made into paper. Bisulphite of calcium is unstable and decomposes readily into neutral sulphite, setting free sulphurous acid. This results in the precipitation of the neutral sulphite on the fibre, which is left harsh even after long washing. Magnesium bisulphite is more stable, and although less corrosive to the fibre, it dissolves the non-cellulose matter even more completely than does the lime salt; further, any sulphate or neutral sulphite which may be formed is easily washed off and the pulp is left soft and white. Sodium bisulphite gives a better product than either of the foregoing, and strong

liquors can be made from it; but it is too expensive for general use.

When the digesters have been filled with the wood chips and the requisite quantity of sulphite liquor is added, the manhole or cover at the top of the digester is securely fastened, and steam is turned on gradually until the pressure reaches seventy or eighty pounds. The cooking is steadily maintained at this pressure for a period of eight to ten hours. At the end of this time the contents of the boiler, consisting of softened pulp, are discharged into large vats and washed. The spent liquor containing the dissolved resinous and non-fibrous portions of the original wood is allowed to drain away from the mass in the tank, which is then washed out and made ready for another charge.

It is the disposition of this spent liquor which constitutes one of the weightiest problems confronting the manufacture of chemical pulps to-day. He is eager to be informed of a means of utilising the liquor that would obviate the present necessity of throwing it into contiguous rivers and streams, for he realises the danger that threatens the industry from the enactment of laws that will prevent him from turning his waste liquors into the watercourses of the country in such large quantities as has been done up to the present time.

By neutralising the liquor and starting fermentation of the contained sugars, alcohol of a low grade is produced from it in several pulp plants in Sweden, and by a patented concentration process used in the United States, a compound is formed from the liquor, named glutrin, which is utilised as a binder in roadmaking, as a tanning extract, and as an adhesive for sand in making moulds and cores for iron castings in foundries.

But the profitable recovery of the organic matter dissolved from wood in the sulphite process is still an unsolved problem. The recovery of the innumerable organic substances dissolved in it, which is so fascinating a field of speculation for the chemist, has no interest for the pulpmaker, and is regarded as something of minor importance compared with the question of getting rid of the liquor in some way agreeable to the authorities and at the same time inexpensively and expeditiously. Although the problem has been deeply studied by able chemists for the past twenty years, it has yet to be tackled by a pharmaceutical chemist, and when it is we may look for the production of a whole series of new organic compounds.

In the soda and the sulphate processes of extraction there is effected a partial recovery of materials. By incinerating the spent soda liquor, after evaporating and concentrating it, the soda itself is regenerated, but there is here again a total loss of the organic derivatives of the wood, which are burned up in recovering the soda.

The soda process is used for soft woods like poplar, cotton, and basswood, whereas the sulphite procsss is exclusively employed for coniferous woods. The chipped wood is boiled in a solution of caustic soda for eight or nine hours at a pressure of seventy or eighty pounds. The pulp produced is soft and bleaches well, making it especially well adapted for the manufacture of book and magazine papers.

Sulphate pulp is prepared by boiling the wood chips in a solution of sodium sulphate containing some caustic soda and sodium carbonate. It is a slower process than either the sulphite or the soda, as the period of boiling, instead of being eight or nine hours, is sometimes extended to thirty-five hours, though good results are possible with a shorter cooking. The sulphate is reduced to sulphide by organic matter during incineration as a step in recovery, and by its presence in the liquor subsequently made oxidation of the fibre is prevented, so that a good yield of strong fibre is obtained. The so-called kraft papers are made by this process, which is not a popular one, as the gases formed have a very offensive odour, which affect the whole neighbourhood of the mill and make the atmosphere almost unendurable to human beings and incapable of supporting plant or vegetable life.

Some of the technical operations of the papermaker afford abundant opportunity for exercise of galenical ingenuity and skill, as, for example, in the sizing of paper to give it a surface resistance to the penetration of liquids like ink, so that the paper may be written or printed on without the ink spreading over the sheet.

In the sizing of newsprint and the common grades of book paper the sizing substance is the ordinary rosin of commerce, which is added in the form of rosin soap to the pulp mass of fibres in the final stages of beating, and precipitated by alum, after the proper proportion of kaolin or china clay has been added (from 5 to 15 per cent) and the yellowish colour of the ground wood has been toned up by the addition of sufficient blue and red aniline dyes or other colours required to impart a white appearance to the finished sheet of paper. In order to insure the perfect distribution of the rosin throughout the paper pulp it is introduced as a liquid soap, made by boiling rosin with soda-ash and adding water, the following being a typical formula:—

Rosin	1350 lbs.
Soda-ash	165 lbs.

Boil for about four hours and just before boiling is completed add about thirty gallons of water. Strain through a No. 80 sieve.

A definite quantity of the soapy emulsion of rosin thus formed is mixed with the contents of the beater, and when it is well distributed, alum is added in sufficient quantity to salt out the rosin and take with it for precipitation into the fibres of the paper pulp the kaolin and other ingredients of the furnish.

It is a disputed question in paper chemistry whether the alum simply throws the rosin out of solution, salts it out, as it were, or combines with it to some extent to form an aluminium resinate. The weight of authority leans to the conclusion that no chemical combination takes place, good results in sizing with rosin having been obtained by the substitution of magnesium sulphate, or diluted sulphuric acid, for alum. At best the salting out process as ordinarily practised is not distinguished by scientific precision, and much more alum appears to be used than is necessary. Alum and rosin when present in excessive amounts cause paper to turn a brownish colour, and it gradually becomes brittle and disintegrates in consequence of the formation of free acids and other chemical changes.

The supply of rosin is not inexhaustible and some scarcity has already developed, and as a consequence of this and a corresponding advance in price, the papermakers are casting about for cheaper substitutes. Besides experimenting with the waste rosins of the rubber industry, an attempt has been made to revive the ancient use of starch as a sizing material, with a fair measure of success as regards ordinary printing papers, but unsuccessfully in the case of writing papers, which require to be almost waterproof in their ink resistance. In this process a compound of starch and aluminium silicate is deposited in the fibres by combining in a cooking operation a partially gelatinised starch with sodium silicate and salting out the mixture with aluminium sulphate.

The more expensive handmade papers are sized with a solution of gelatin, the sheets being dipped separately into a tub of the size and afterward hung up to dry, being finally pressed between zinc plates. In another process now more generally used the sheets of paper are carried by travelling felts through a bath of heated size, the excess gelatin being removed by the action of rubber or wooden rollers through which the papers are passed before leaving the apparatus, and the drying is effected on an extension of the machine. With the ordinary machine-made writing paper, however, the sizing material is mixed with the pulp in the beating engine, as in the case of newsprint and book paper, and there interlocked with the fibres by the alum salting out process previously described.

It is expected of the pharmacist that he should be well informed regarding methods of determining the quality of

paper by microscopical and chemical tests at least—physical methods may be left to the experienced paper-maker or dealer, who is often able to make a shrewd guess at the composition of a paper by the mere appearance and feel of the finished product.

In "taking the fibre count," as the method of estimating the proportion of pulps in a paper is termed, the use of a staining agent is necessary, all vegetable fibres being transparent and nearly colourless. The best stain for this purpose is Herzberg's chlorzinciodine solution, which is made up as follows:—

Solution A.

Zinc chloride	20 grms.
Distilled water	10 cc.

Dissolve.

Solution B.

Potassium iodide	2·1 grms.
Iodine crystals	0·1 „
Distilled water	5·0 cc.

Dissolve.

Dissolve A by adding the water to the zinc chloride in a beaker.

Dissolve B by adding a few drops of the water to the potassium iodide and iodine crystals in a glass beaker and after dissolving add the remainder of the 5 cc. of water.

The two solutions—A and B—are then mixed together and allowed to stand for twenty-four hours to settle, after which the clear liquid may be poured off into amber glass bottles fitted with dropping stoppers.

A drop of Herzberg's stain applied to the paper pulp on a microscope slide brings out a wine-red colour on cotton and linen fibres, gives a good clear blue colour with bleached soda and sulphite woodpulps and a characteristic yellow or greenish grey-yellow with ground or mechanical woodpulp.

The following method of preparing a sample of paper for the microscope is used by the Bureau of Standards, Washington, D.C.:—

Several small pieces of paper of about the area of a cent are cut from different parts of the sheet of paper; these pieces are then placed in a beaker and covered with some ½ per cent caustic soda solution, and the whole mass is then brought to a boiling over a suitable heating device. After boiling for about a minute some tap water is added to wash out the caustic soda, followed by two or three drops of a 25 per cent solution of hydrochloric acid to neutralise the alkali.

The slightly acid solution is then poured off and enough of the small pieces of paper are pinched off and rolled into a ball of about the size of a pea. This small ball of pulp should be well rolled between the thumb and finger and then placed in a test-tube and the test-tube half filled with water. The test-tube is then shaken vigorously until the paper has been entirely broken up and the fibres are well separated. A small portion of the pulp is then carefully removed on the point of the microscope needle from the test-tube and placed on each end of one of the microscope slides, the excess liquid being removed by a pointed strip of filter paper brought in contact with the edge of the drop.

The fibres forming the pulp are thoroughly dried and a drop of the Herzberg stain is added, then the fibres are well "teased" out by the use of the microscope needles, a cover glass is placed over them and well pressed down, all the stain pressed out around the edges of the glass being removed with filter paper.

The slide is next placed under the microscope, and after studying the various fields an estimate of the proportion of each of the various kinds of fibres may be given.

One of the most frequently used solutions for staining fibres for microscopic examination is a solution of iodine in potassium iodide of the following composition:—

Iodine	1·15 grm.
Glycerin	1·0 „
Potassium iodide	2·0 „
Water	20·0 „

In contact with this solution cotton, linen, bleached hemp, and ramie fibres are coloured brown; while mechanical woodpulp, jute, and manilla hemp are coloured yellow or yellow-brown. Chemical pulp of wood, straw, and esparto are not affected.

A solution of calcium nitrate in iodo-potassium iodide is said to offer some advantages over chlorzinciodine solution. For one thing it does not absorb moisture from the air, and it does not alter the fibres. It is made as follows:—

Solution No. 1.

Nitrate of calcium crystals ..	100 grms.
Distilled water..	50 „

Dissolve.

Solution No. 2.

Iodine	1 grm.
Potassium iodide	5 „
Distilled water..	90 „

Dissolve.

For use 3 cc. of Solution No. 1 is added to Solution No. 2.

This solution stains linen fibre a rose colour with a brownish tinge; ground wood is coloured yellow; bleached sulphite fibre, a delicate rose tint; unbleached sulphite fibre, clear yellow; soda poplar fibre, indigo blue; straw fibre and esparto blue.

Several rough identity or diagnostic tests for the presence of ground wood in paper are employed by paper dealers, of which the following may be noted:—

A solution of phloroglucin in alcohol is used for identifying mechanical or woodpulp, which turns a beautiful red colour in contact with the reagent, the depth of tint, as compared with Schopper's standard colour tables, corresponding to the amount of mechanical pulp, or lignified fibre, present. The procedure is as follows:—

Into a flat porcelain dish pour 2 parts of a 2 per cent alcoholic solution of phloroglucin and 1 part of hydrochloric acid (phloroglucin, 1 grm.; alcohol, 50 cc.; hydrochloric acid, 25 cc.), and immerse in the solution the paper under examination. After ten minutes of contact compare the colour developed with Schopper's standard colour table.

In papers having a red or rose colour the phloroglucin reaction breaks down and the employment of benzidine hydrochloride is recommended, this reagent giving rise to an orange colour in the presence of mechanical woodpulp. The reagent is made by rubbing up 15 grains of chemically pure benzidine with 15 minims of hydrochloric acid and dissolving the benzidine hydrochloride formed in 2½ drms. of water at 122° F. The solution is simply dabbed on the paper to be tested, and the orange colour produced in the presence of mechanical woodpulp is the more intensive the more woodpulp is contained in the paper. The test is a very delicate one, the orange colour being produced even when only traces of mechanical woodpulp are present.

Aniline sulphate stains lignified fibre yellow, and a 10 per cent solution of this salt, acidulated with sulphuric acid, imparts a golden yellow tint to paper containing ground wood, the colour being more or less intense according to the proportion of ground woodpulp present. A solution of aniline chloride and hydrochloric acid is also used, but the results with each of these aniline solutions are inferior to those obtained with phloroglucin.

Wurster's reagent is popular in Germany as a diagnostic test for ground woodpulp, but as it, as well as phloroglucin and the aniline salts, develop their characteristic colours with any lignified fibre, the test is not conclusive of the presence of ground woodpulp alone. Wurster's reagent consists of a 50 per cent solution of dimethylparaphenylenediamide in water. It gives a deep red colour

with ground woodpulp. There are now available test-papers impregnated with Wurster's reagent which are called "di-paper" for convenience. Strips of this test-paper are placed in a double sheet between the paper to be tested. After moistening the layers of paper with water the red colour that develops is compared with a standard table of colour values which is sold with the test-papers.

It is the lignocelluloses, reacting to the foregoing reagents, which impart the greatest element of weakness and decay to paper. They are unsaturated compounds greedy of oxygen and profoundly affected by all oxidising agents. Pure cellulose is a saturated compound which is resistant to the action of both chemicals and atmospheric changes, and this accounts for the practical indestructibility of rag papers, which are free from lignin, and consist of nearly pure cellulose. Books and papers dating from the middle ages are to be found in museums and libraries to-day in a good state of preservation because they were made at a time when rags were the only crude material for the manufacture of paper.—*The Chemical Engineer*, xviii., No. 4 (from *Paper*).

THE SCIENTIFIC WEEK.

(*From Our Paris Correspondent*).

Keep Your Fluorine as Long as Possible.

Professor Armand Gautier has continued the explanation of the researches that, in collaboration with M. Clausmann, he has undertaken concerning the fluorine in the organism.

The authors have discovered that for 100 grms. of substance there exists 3·04 mgrms. of fluorine in the brain of a man; in the brain of an ox 3·46 mgrms.; in the human lungs, 2·44; in the thymus of a young lamb, 8·48; in the kidney of a man, 2·30, &c. These quantities, although very weak, are sufficient to explain the rôle of the fluorine, which, as M. Armand Gautier established recently, is necessary for the assimilation of phosphorus. These last experiments have likewise confirmed this remark that fluorine diminishes as the organism grows older.

Pieces of Money and Hygiene.

In order to avoid disputes, most of the tramcar and autobus conductors have a habit of holding, between their teeth, the coins for which they have to give change. The Council of Hygiene of Rome has received many complaints concerning this habit, and certain experiments, tried under its direction, have shown, it appears, that if banknotes are laden with bacteria, the copper, silver, and gold coins are practically *aseptic*, on account of the bactericidal action of the metallic salts and oxides formed on their surface. On the other hand, it was declared that nickel coins did not enjoy this same property precisely on account of their unalterability.

But the conclusions of the learned Italians are not accepted in France. M. Langlois, Director of Science, has washed several pieces of money, more or less worn, in a determined quantity of sterilised water, and the averages of his numerations for each series of coins have reached the following figures for each cubic centimetre of the washing water:—

10 c. Copper	coins,	760,000 bacteria,	3	p.c. mould.
25 c. Nickel	,,	140,000 ,,	2	,, ,,
2 fr. Silver	,,	160,000 ,,	1	,, ,,
25 fr. Gold	,,	220,000 ,,	0	,, ,,
Banknotes	..	1,200,000 ,,	8	,, ,,

Among the bacteria the most frequently met with are—Sarcines, Bacillis subtilis, Staphylococcus, Pneumobacillus, Bacillus liquefaciens; amongst the moulds by the side of diverse Penicillium, the terrible Aspergillus niger.

The experiments of M. Langlois indicate that if pieces of money constitute a bad centre of culture for bacteria, they transport, nevertheless, very dangerous species in alarming numbers.

The adoption of nickel money constitutes a very appreciable progress, since the washings of several pieces of 25 c. gave the lowest average. On the other hand, the banknotes are particularly rich in bacteria.

The water in which had been washed a very much worn French fifty franc banknote supplied more than three millions of microbes. That used for washing a nearly thousand franc banknote gave only 270,000.

A Mammoth in Flesh and Bones.

"L'Anthropologie," by the pen of its director, Professor Boule, informs us of the precious acquisition just made by the Paris Natural History Museum of a mammoth with its soft parts partially preserved. This magnificent example has been offered to the Museum by Count Stenbock-Fermor, who had it extracted at his own expense from one of the islands of New Siberia, and brought it to Europe by sledge, boat, and railway. It is probably the only example that will ever be seen in central Europe, for subsequently to the gift of Count Stenbock-Fermor an imperial ukase has forbidden any further exportation of mammoths either whole or in parts.

It is known that these fossils preserved in the ice were perceived in 1806 (Adam, Mouth of Lena), but the only mammoth preserved in these conditions and brought to Europe is to be seen in the Museum of the Academy of Science of St. Petersburg. The anatomy of the soft parts, its histology, the study of the blood, have constituted, on the part of the Russian *savants*, a palæontological work of a kind evidently quite new, presenting, at least, a lively interest of curiosity.

The sample at the Paris Museum of Natural History is sufficiently well preserved to allow of like studies. They are already begun.

The whole animal and its soft parts will shortly be exposed to the public; it will form a new attraction to the great scientific establishment. The public will doubtlessly contemplate with a lively interest, besides the skeleton, of which the skull notably is perfectly preserved, a large part of the skin covered with its hair, the tail, and a whole ear.

Vegetables Manufacture Urea.

Urea has long been considered as characteristic of the desassimilation of animal albuminoids. However, there has been some found in mushrooms. Recently, M. Fosse in analysing a rather large number of vegetables, has remarked that urea is to be met with very generally in the vegetable kingdom—carrots and potatoes. What is to be deduced from this presence of urea? Can it be considered as a physiological product of the vegetable cell, or has it simply been drawn by the roots from the soil where it is always to be met with in more or less important quantities?

The experiments have shown that it could really be considered as a product of the activity of the vegetables cells. By cultivating moulds such as *Aspergillus niger* and *Penicillium glaucum* in aseptic conditions and on definite media containing sugar and ammonia, it has been stated that these moulds really produced urea. Likewise, in treating the higher classes of vegetables, wheat, barley, Indian corn, peas, clover, and beans, M. Fosse has been able to show that in these plants also urea was formed in the course of germination, when the embryo then growing consumes the reserve material contained in the grain. Like animals, vegetables are then susceptible of producing urea.

The Survival of Congealed Fish.

The experiments performed some time ago by Professor Raoul Pictet have shown that living fish might be con-

gealed without being killed, provided that the freezing process was performed in a very slow manner. When the fish is fixed in the block of ice, it is noticed that its tissues can be pounded as ice is pounded. If at the end of a certain time the block of ice is thawed very slowly, it is remarked that when the water is melted, the fish gradually regained their activity, and after some time they swim about as if nothing had happened.

It is in taking these facts as a basis that MM. Mir and Audigé have established the principle of a process by which it is possible to transport to a distance fish living but congealed. The blocks of ice containing the congealed fish could be transported in frigorific wagons at 0°.

This process is much more economical than that which exists on certain railways, notably in Germany and Austria, and which consists in transporting the living fish in water. In this case it is necessary to employ a relatively large quantity of water. To transport one kilogrm. of carp, four or five litres of water are required, and for the same weight of trout from 10 to 20 litres of water are necessary. A wagon that can only carry 10,000 kilogrms. would be able to transport only 500 to 1000 living trout.

The process indicated above by MM. Mir and Audigé is infinitely more simple and less costly. It cannot fail to interest the hygienist.

THE SYNTHESIS OF VEGETABLE MATTER.

M. Daniel Berthelot, Professor at the Higher School of Pharmacy, and M. Gaudichon have just communicated to the Academy of Sciences the continuation of their researches on the synthesis of vegetable matter by light, thanks to the gases of the air. By exposing carbonic acid and the amount of water contained in the atmosphere to the ultra violet irradiation of the mercury lamp they have obtained both formic acid, the simplest of vegetable acids, and formaldehyde, which is the point of departure of sweet matters and of celluloses.

These reactions which take place in plants, in the sun, only under the influence of diastases, is realised here in vitro, thanks to the accelerating catalytic power of the ultra-violet light.

THE ACTION OF ULTRA-VIOLET RAYS.

Professor Hunneguy has presented before the Academy of Sciences a very interesting note concerning the action of ultra-violet rays on the development of the egg of the "Ascaris" or Ascarides.

We are acquainted with the first manifestations of life only from the observation of the eggs of the lower animal life. As soon as it is fertilised the egg is segmented into two parts, then into four, then eight, and so on. The ultra-violet rays slacken this segmentation of the egg, and this slackening is proportional to the quantity of energy received.

INTERESTING GRAFTING.

In a certain number of cases (18 out of 100 trials) M. Daniel has managed to graft the root of a carrot on to the root of another umbelliferous plant, the peppery fennel.

The carrot (a semi-red Nantes type) has a tuberculous red root, giving out a special smell and having a sweet taste. The peppery fennel has a white root, not very sweet, with a special smell and a pungent peppery taste.

The roots of the grafted carrots became tuberculised, their colour was red but mixed frequently with green or brown. So then the colouring of the grafted tubercle was modified, but, on the other hand, the red pigment of the carrot did not pass into the fennel,

The smell of the grafted carrots was also modified; moreover they were not so sweet, and had, though in a less degree, the taste of the root of the fennel. The carrot thus loses its alimentary value. What is interesting to note is that the exchanges between the graft and the subject are localised to such and such a substance and are not produced in the same manner on both sides.

NOTICES OF BOOKS.

Allen's Commercial Organic Analysis. Volume VII. Fourth Edition. Edited by W. A. DAVIS, B.Sc., A.C.G.I., and SAMUEL S. SADTLER, S.B. London: J. and A. Churchill. 1913.

THE seventh volume of the fourth edition of "Allen's Commercial Organic Analysis" deals with the Vegetable Alkaloids, Glucosides, Animal Bases, and Acids, &c. As our knowledge of these subjects has rapidly advanced in recent years the text has had to be thoroughly revised, and many amplifications and corrections have been made. As far as possible the old arrangement and classification have been preserved. The section on Animal Bases, which has been re-written, and which gives an admirable survey of the analytical methods employed in their identification, is from the pen of Prof. A. E. Taylor, of the University of Pennsylvania.

Lectures on Chemistry in Gas-works. By W. J. A. BUTTERFIELD. London: The Institute of Chemistry of Great Britain and Ireland. 1913.

THE two lectures which this booklet contains were delivered before the Institute of Chemistry in December and January, 1912-13, and were intended to give students and gas-works' chemists some idea of the nature of the work which they should be qualified to perform. The first lecture dealt with the requirements of a public gas supply, the consumption of gas in different countries and cities, and the evolution of modern methods of gas making from the earliest processes. In the second lecture the lecturer discussed the cleaning of gas, the recovery of nitrogenous products from coal, and the chief by-products. The analytical work which the gas-works' chemist will be called upon to carry out is outlined, and a high ideal of efficiency, alertness, and skill is put before him; in the lecturer's opinion he should be possessed of a special knowledge of the chemistry of fuels, and in addition should have a thorough acquaintance with the principles of mechanics and physics.

Über die Aufnahme der Radium—Emanation durch das Blut. ("The Absorption of Radium Emanation by the Blood"). By C. RAMSAUER and H. HOLTHUSEN. Heidelberg: Carl Winter. 1913.

THE research described in this monograph was performed at the Radiological Institute attached to the University of Heidelberg, and has brought to light some facts of first-rate importance in medical and biological science. By means of a new method of measuring the absorption coefficients of the blood for radium emanation it has been definitely proved that the coefficient is double that of water at the same temperature; thus some of the very contradictory statements to be found in literature may at last be regarded as conclusively refuted. It has also been proved that the red blood corpuscles are the chief carriers of the emanation, and the validity of Henry's Law has been established between very wide limits.

Handbuch der Arbeitsmethoden in der Anorganischen Chemie. ("Handbook of Practical Methods of Inorganic Chemistry"). Edited by Dr. ARTHUR STAHLER. Volume I. Leipzig: Veit and Co. 1913. (M. 25).

DIRECTORS of laboratories and chemical demonstrators will find in this book much information which will be of great value to them. It is not always easy to obtain details of the latest forms of apparatus and of the best methods of carrying out special operations, such as are to be found here, and the text-books hitherto existing have not attempted to attain to the comprehensiveness at which the many collaborators who have written this book have aimed. In Volume I. the laboratory and its equipment are described, with illustrations of many kinds of apparatus, including the latest modifications and improvements.

Mechanical operations such as separation by filtration, centrifugation, &c., are also described, and valuable sections deal with the preparation and fitting up of apparatus and the making and storing of reagents. The actions of reagents on glass and the advantages of the use of quartz and other glasses are discussed. The section on the electrical apparatus employed in chemical work will be found exceedingly useful, providing as it does enough details for all ordinary purposes.

Die Gasglühlichtbeleuchtung in ihrer Entwicklung und Bedeutung. ("Incandescent Gas Lighting: Its Development and Importance"). By Dr. C. Richard Böhm. Charlottenburg: Gustav Heydenreich. 1913.

This little pamphlet has been re-written for the general public, and aims at giving a brief readable account of the use of the incandescent mantle in lighting by gas. Interesting details and illustrations of the first gas works built in 1825 in Berlin are given, and the evolution of the incandescent burner is traced. Those who are interested in questions of illumination will find that the pamphlet contains matter relating to the efficiency and expense of different systems which is worthy of their attention.

CORRESPONDENCE.

ATICONIC ACID.

To the Editor of the Chemical News.

Sir,—We have sometimes wondered why discoveries in science find their way so slowly into the text-books. As an illustration, in 1893 Dr. Arthur Brooke, in collaboration with Prof. Rudolph Fittig, in the Chemical Laboratory of the University of Strassburg, discovered a new isomeric unsaturated acid, to which they gave the name *aticonic*, because it more closely resembles itaconic acid than it does the other isomers, mesaconic and citraconic. This was considered at the time quite a brilliant and important discovery, and it received due consideration in the *Annalen* and other journals during the year in which the synthesis was effected.

In the summer of 1894, Prof. Fittig was honoured with an invitation by the German Chemical Society to read a paper descriptive of his work on the unsaturated acids, and naturally the newly discovered one was given prominent attention. The full text of this address was published in the *Berichte* of September, 1894.

An examination of fifteen or eighteen recent text-books on organic chemistry failed to show any mention of aticonic acid, although the other three isomers were described. These were German, English, and American works. One author of a widely used and well known text book, when his attention was called to the omission, said that in a brief work one could not include everything, and so he omitted aticonic acid, although he gave the other three a prominent place.

Is it possible that our text-book writers copy from each other, and do not sufficiently consider the original sources? —I am, &c.,

Nicholas Knight.

Cornell College, Mount Vernon,
Iowa, July 9, 1913.

Literary Intelligence.—Messrs. J. and A. Churchill, of 7, Great Marlborough Street, W., have nearly ready for publication the Seventh Edition of "The Microtomist's Vade-mecum," by A. Bolles Lee; the Sixth Edition of the late Prof. Campbell Brown's "Practical Chemistry," edited by Dr. Bengough; and the Third Edition of a Text-book of Physics," edited by A. Wilmer Duff.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Atti della Reale Accademia dei Lincei.
Vol. xxii. [1.], No. 6, 1913.

Polyazoxy Compounds.—A. Angeli.—When Mills's diazobenzene, $C_6H_5N_2.C_6H_4.N_2.C_6H_5$, is suspended in glacial acetic acid and heated on the water-bath with 30 per cent hydrogen peroxide, a bisazoxybenzene of formula

$$C_6H_5.\underset{\substack{\| \\ O}}{N}=N.C_6H_4.\underset{\substack{\| \\ O}}{N}=N.C_6H_5$$

is obtained. The azoxy compound, $C_6H_5.N_2.C_6H_4.N_2O.C_6H_4.N_2.C_6H_5$, is prepared by acting with sodium alcoholate on paranitrobenzene. It yields triazoxybenzene when treated with H_2O_2. Following are the characteristic properties of the three azoxy compounds:—

Azoxybenzene—Melting-point, 36°; colour, light yellow; coloration with H_2SO_4 at 100°, orange-red; with Br gives bromo-derivative.
Bisazoxybenzene—Melting-point, 155°; Colour, dark yellow; coloration with H_2SO_4 at 100°, violet; with Br gives dibromo-derivative.
Triazoxybenzene - Melting-point, 230°; colour, golden yellow; coloration with H_2SO_4 at 100°, blue; with Br gives dibromo-derivative.

Vol. xxii., [i], No. 7, 1913.

Electrolysis of Crystalline Compounds.—G. Bruni and G. Scarpa.—The authors have studied the electrolysis of silver iodide, using silver electrodes, and by six experiments performed at different temperatures, viz., 160°, 200°, 250°, 300°, and 400° (two experiments), have proved that the quantity of silver which migrates from the anode to the cathode follows Faraday's Law.

Hydrogenation of Santonine in Presence of Palladium Black.—G. Bargellini.—In presence of palladium black santonine, when it absorbs the quantity of hydrogen calculated for 2 atoms, is transformed into a dihydrosantonine, which with alcoholic potash gives a yellow coloration and a green fluorescence. This compound has a ketonic character, and yields a semicarbazone. When santonine, in presence of palladium black, absorbs the quantity of hydrogen calculated for 4 atoms it is converted into a tetrahydrosantonine, which yields no coloration with alcoholic potash. At the ordinary temperature and at a pressure of about an atmosphere santonine does not absorb more than 4 atoms of hydrogen.

MISCELLANEOUS.

Three New Alloys.—In their last official report as chemists to the American Institute of Metals, Arthur D. Little, Inc., of Boston, mention three new alloys among the various items of recent progress in the metal industry. A French patent has recently been issued covering the production of two types of alloys from copper, zinc, and silicon, which are claimed to possess great tenacity, resistance to acids and alkalis, and to be capable of rolling into finished shapes. Another new alloy has been patented by the Ajax Metal Company, composed of iron, nickel, and copper, which is claimed to be non-corrosive, malleable, of great tensile strength, and capable of being rolled, drawn, or cast. A new type of pyrophoric alloy has been patented in Germany which consists of the addition of 5 per cent metallic cerium to an alloy of manganese and antimony. The inventor claims excellent pyrophoric properties from this alloy, which is essentially different from the other alloys of this type in which cerium is the main source of the pyrophoric characteristics.—*Chemical Engineer*, xvii., No. 4.

THE CHEMICAL NEWS.

Vol. CVIII., No. 2801.

THE CHEMICAL AFFINITIES OF NITROGEN.

By GEOFFREY MARTIN, Ph.D., M.Sc., B.Sc.

Nitrogen has long been regarded as an element possessed of very feeble affinities, and consequently the recent remarkable experiments of Strutt and collaborators on "Chemically Active Nitrogen" (*Proc. Roy. Soc.*, 1911, A, lxxxv., 219, 377; lxxxvi., 56, 262; lxxxvii., 179; *Nature*, May 15, 1913, p. 283), which revealed the possibility of nitrogen possessing strong affinities, came as a very surprising result to many chemists.

It seems, however, to be quite overlooked that the present writer no less than eight years ago in his book "Researches on the Affinities of the Elements" (published by Churchill, 1905), showed from a study of the affinities of the successive elements of the periodic system that nitrogen, owing to its position in the periodic system, must possess very strong affinities.

This result was arrived at by studying the manner in which the affinities of the successive elements altered as we went down the series Li, Be, B, C, N, O, F, and the writer then finally concluded that it is quite incorrect to speak of chemically active and inactive elements, but that practically all the elements investigated have their strong and weak affinities, only sometimes these strong affinities are exerted on well known elements—when we call the element "chemically active"—and sometimes on rare elements—when we call the element "inactive."

As the result of the study of the compounds of nitrogen and the compounds of neighbouring elements the writer showed that nitrogen, just like sodium or chlorine, possesses very strong affinities for some elements and very weak ones for other elements, but that its affinities were masked by three causes:—

(1) The elements for which it exhibits its strongest affinities are those which have the power of self-combination most strongly developed.
(2) That nitrogen itself has the power of self-combination strongly developed.
(3) That the elements for which nitrogen exhibits its maximum affinities are all somewhat uncommon in a chemical laboratory, and so the chemical activities of nitrogen are not brought prominently before the eyes of chemists.

All these causes *lower* the apparent power of entering into chemical combination of nitrogen, and have led chemists to almost universally regard nitrogen as very inert chemically.

Strutt's experiments revealing the chemical activity of nitrogen are, in fact, a remarkable fresh confirmation of the properties that I showed nitrogen to possess some eight years ago, and as Dr. Strutt refers back to Faraday (*Nature*, May 15, 1913, p. 285) for a vague prophesy in this direction, and appears to be quite unaware of my own results—arrived at by means of a laborious study of known compounds—I think that I can justly claim that I was the first who showed that *from its position in the periodic system* nitrogen *must* be an element possessing strong affinities, and also simultaneously clearly indicating what elements these affinities would be most strongly exerted upon.

As these results of mine appear to have been quite overlooked by current writers, and have considerable interest at the present time when atmospheric nitrogen is being fixed on an enormous scale commercially, I venture to bring my results once more before the chemical world.

The following is my method of investigating the magnitude and nature of the affinities which the elements Li, Be, B, C, N, O, F, exhibit in succession for the other elements of the periodic system. First of all I construct the periodic system of elements in the usual way, confining myself, however, solely to the elements of the even series, thus:—

Li	Be	B	C	N	O	F	Ne
Na	Mg	Al	Si	P	S	Cl	Ar
Cu	Zn	Ga	Ge	As	Se	Br	Kr
Ag	Cd	In	Sn	Sb	Te	I	Xe
Au	Hg	Tl	Pb	Bi	—	—	—

Suppose, now, I wish to investigate the affinities which a given element A exhibits towards these various elements. I first of all undertake a study of the relative stability of the compounds which A produces with each of the elements of the above table, especially as regards the magnitude of the heat of formation, stability towards temperature, power of being reduced, &c.; from

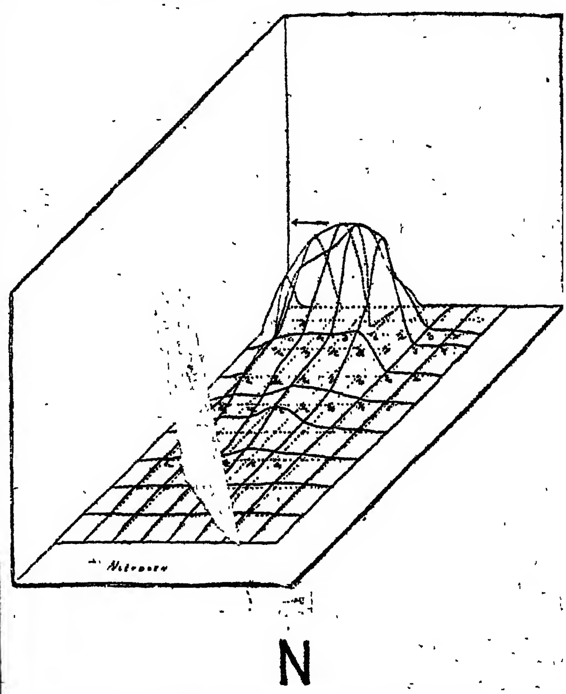


Fig. 1.—Affinity Surface for Nitrogen.

Showing at a glance how the Affinities of Nitrogen for the various Elements of the Periodic System vary. (Taken from the writer's book, "Researches on the Affinities of the Elements").

such a comparative study it is possible to arrive at a very good idea of the relative strengths of the attractive forces which the element A exerts on each of the above elements.

Next from *each* of the elements of the above table I erect a perpendicular *proportional* to the chemical attraction or affinity which it possesses for the given element A.

A surface is then described through the summits of these perpendiculars, and we get what I call the "affinity surface" of the element A, in respect to the other elements of the periodic system.

The shape of this surface shows at a glance the relative magnitude of the affinities exerted on the different elements of the periodic system.

The details of constructing these surfaces, together with all the data on which the results are founded, is collected together in the writer's book, "Researches on the Affinities of the Elements," and I do not propose to go further into

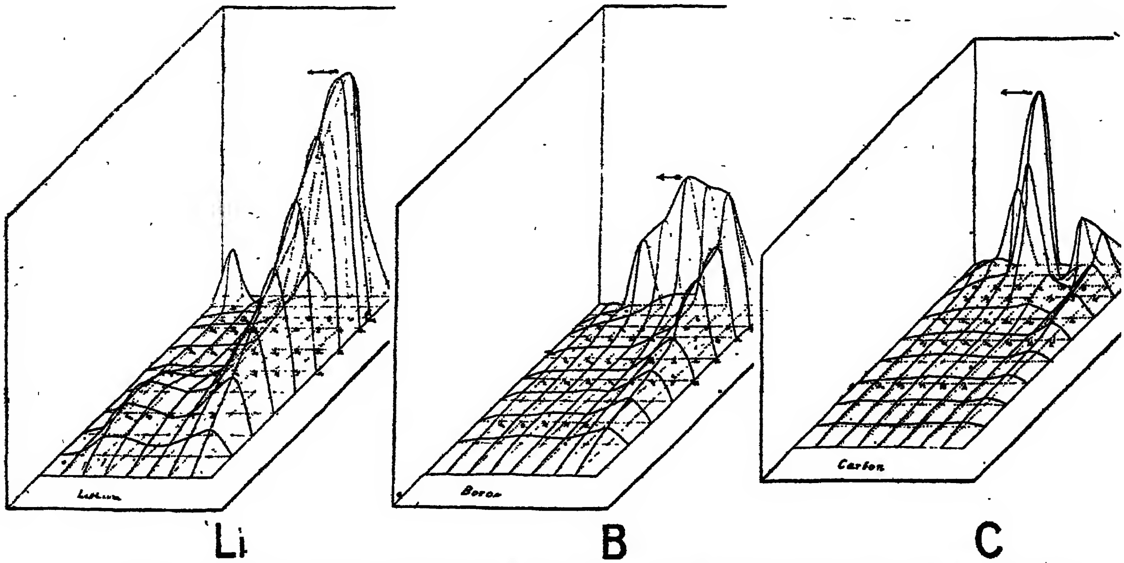


FIG. 2.—Showing how the Affinities of the successive Elements vary as we pass from Lithium

this matter here, because a detailed study of the individual compounds formed by each of the thirty-seven elements of the above table with the other elements requires a very large space for discussion, and indeed a volume of some hundreds of pages was necessary for the purpose. As this data is collected together in the above-mentioned book, I will here only apply the results obtained from a study of the affinity surfaces of the successive elements of the first two cycles of the periodic system to nitrogen so as to show that we should expect nitrogen to exhibit very strong affinities for some elements and weak ones for other elements, just as the other elements of the periodic system do.

Fig. 1 shows the form that the affinity surface assumes for nitrogen.

Description of the Affinity Surface for Nitrogen.

The numbers given refer to the heights of the perpendiculars erected from the various elements below mentioned as proportional to the affinity that nitrogen possesses for them.

Cross Sections.

Li, Be, B, C, N, O, F.—The affinity for nitrogen rises from Li to B, then falls, attaining a minimum at C, rises again at N, and then falls, becoming very small at F.

Li 4·1, Be 5, B 8, C 0·5, N 4, O 0·2, F 0·1.

Na, Mg, Al, Si, P, S, Cl.—The affinity for N is very small at Na, rises steadily, attaining a maximum at P, then falls again, becoming very small at Cl.

Na 1, Mg 6, Al 7, Si 9, P 11, S 0·2, Cl 0·1.

Cu, Zn, Ga, Ge, As, Se, Br.—The attraction is very small for Cu, rising as we pass from Cu to Zn, and it remains appreciable until As is reached, then falling it becomes very small for Se, and still smaller for Br.

Cu 0·4, Zn 3, Ga 3, Ge 3, As 3, Se 0·2, Br 0·1.

Ag, Cd, In, Sn, Sb, Te, I.—The affinity is small for Ag and Cd. It is unknown for In, Sn, Sb, but probably rises from Ag to Sb; for Sb it is very small, and is still smaller for I.

Ag 0·3, Cd 2·5, In 2·5, Sn 2·5, Sb 1·0, Te 0·2, I 0·15.

Au, Hg, Tl, Pb, Bi.—The attraction for nitrogen is very small for these elements.

Au 0·1, Hg 0·2, Tl 0·2, Pb 0·2, Bi 0·2.

Longitudinal Sections.

H, Li, Na, Cl, Au.—The attraction for N increases from H to Li and then steadily decreases until Au is reached.

H 1, Li 4·1, Na 1·0, Cu 0·4, Ag 0·3, Au 0·2.

Be, Mg, Zn, Cd, Hg.—The attraction for N in the case of Be is unknown, but probably it is greater than in the case of Mg; the affinity probably reaches a maximum in the case of Mg and then sinks, becoming very small for Hg.

Be 7, Mg 6, Zn 3, Cd 5·5, Tl 0·2.

B, Al, Ga, In, Tl.—The attraction for N at B is very great, and sinks thence to Al; the affinity of N for the other elements is unknown, but probably sinks steadily from B to Tl.

B 8, Al 7, Ga 3, In 2·5, Tl 0·2.

C, Si, Ge, Sn, Pb.—The affinity for N is very feeble at C, but it rises greatly as we pass from C to N; for the other elements it is unknown, but probably sinks rapidly from C to Pb.

C 0·5, Si 9·0, Ge 3·0, Sn 2·5, Pb 0·2.

N, P, As, Sb, Bi.—The attraction for N rises rapidly from N to P; the attraction for N of the other elements is unknown, but probably is feeble, falling from As to Bi.

N 4, P 8, As 3, Sb 1, Bi 0·5.

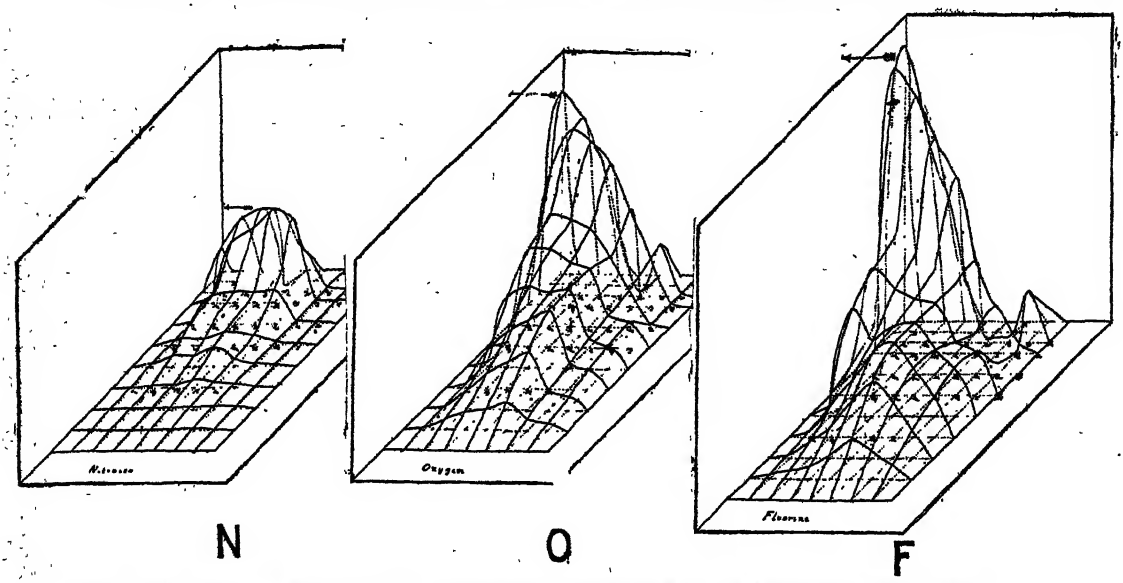
O, S, Se, Te.—The affinity for N is small all through the series, sinking from O to S, remaining about the same for Se as for S, then rising somewhat for Te.

O 0·2, S 0·2, Se 0·2, Te 0·3.

F, Cl, Br, I.—The attraction for N is very small for all these elements, being greatest for I and least for F.

F 0·1, Cl 0·1, Br 0·1, I 0·15.

Now let us compare these affinities of nitrogen with those of neighbouring elements. If we arrange in order the affinity surfaces of the first series of elements of the periodic system (viz., Li, Be, B, C, N, O, F), a remarkable fact becomes apparent, which is illustrated in Fig. 2. The affinity surfaces of the successive elements assume the appearance of successive positions of an advancing wave, whose crest appears on the extreme right hand side of the diagram in the case of Li, and then sweeps from right to left as we pass from Li towards F, until at F the crest is on the extreme left-hand side (see Fig. 2).



towards Fluorine. (Taken from the Author's book, "Researches on the Affinities of the Elements").

The same phenomenon appears with the elements of the second (Na, Mg, Al, Si, P, S, Cl, Ar) cycle, and later cycles of the periodic law, only in most cases the wave form seems to pass more or less discontinuously from right left, and *there often seems to be a depression at the elements of the fourth group, probably an apparent effect due to the abnormally developed power of self-combination possessed by these elements.* For example, when we come to compare the heats of formation of the two oxides of carbon, we have, according to Thomsen, the following numbers :—

$$(C, O) = 29,000 \text{ cal.},$$
$$(CO, O) = 67,960 \text{ cal.},$$

so that the addition of the second atom of oxygen to the carbon atom is attended with the liberation of a far greater quantity of visible heat than the addition of the first atom. This is a remarkable result, quite at variance with the usual rule (see "Affinities of the Elements," p. 241 *et seq.*) which holds in chemistry, and the explanation is, probably, that the small quantity of heat evolved in the formation of CO is due to the fact that before an oxygen atom can combine at all with a carbon atom it has to separate it from its combinations with other carbon atoms. The carbon atoms attract each other very strongly indeed, as is shown not only by their great power of self-combination, but also by the great hardness and involatility of certain forms of carbon. Consequently this initial separation of the carbon atoms absorbs a very large quantity of heat, and this lowers the apparent heat of formation of CO to much below its real value.

In gaseous CO, however, the carbon atoms are already separated, and so no further great quantity of heat is absorbed before the additional O can be added on to form CO_2. It is very probable, therefore, that the apparent heats of formation and stability of the oxides, and indeed of all other compounds of carbon, are very much below their real values on account of the exceptionally large quantities of heat absorbed in separating the carbon atoms from each other. This is probably the reason why the heat of formation of CH_4 is less than the heat of formation of SiH_4, although CH_4 is a much more stable body than SiH_4.

Silicon is the element next to carbon which possesses to the greatest extent the power of self-combination. The apparent heat of formation of its oxide is also, therefore, probably much less than its true value. In the case of certain monatomic atoms, such as those of sodium, mercury, &c., and of elements in which the power of self-combination is but slightly developed, the apparent heats of formation probably correspond fairly closely with the real heats of formation.

We should therefore expect that when we come to compare the thermal data and stability of the compounds of the various elements we will find that *there is an apparent general depression very much below their true values as we approach such elements as carbon and silicon which lie in the middle of a cycle of elements of the periodic system where the power of self-combination is largely developed;* whereas there should be nearly correct values for such elements as Na, Hg, &c., which lie on the extreme borders of the cycle of elements, and where the power of self-combination is but feebly developed. A glance of the relative magnitudes of the affinity surfaces of the successive elements exhibited in Fig. 2 shows that this is actually the case.

Applying these results to the affinity surface of nitrogen we will now show that *the chemical inactivity of nitrogen is to a great extent only an apparent effect.*

A study of the affinity surface for nitrogen shows that the point of maximum chemical affinity lies over boron.

When we contrast the nitrogen affinity surface with those of Na or Cl, it becomes manifest that while Na expends its energies upon elements belonging to the later groups of the periodic system (viz., O, S, Se, F, Cl, Br, I), and has little affinity for elements of the earlier groups (such as the alkali metals and alkali earth metals), and that while chlorine expends its energies principally upon the elements of the early groups of the periodic system (such as the alkali metals and alkaline earth metals), but has little affinity for elements of later groups (such as the halogens and oxygen group of elements) that, in contradistinction to these, *nitrogen expends its energies on elements of intermediate groups—principally on those of Groups* III., IV., *and* V.—*but has little affinity for those of earlier or later groups (such as the alkali elements and the halogens).* For example, its combinations with boron, silicon, and phosphorus are quite remarkable by reason of their great stability. The phosphide P_3N_2 must be heated in oxygen gas to a temperature above that at

which hard glass melts, before the oxygen begins to act on it! When we consider the great attraction that phosphorus has for oxygen, this shows that the affinities that nitrogen exerts on phosphorus are very great.

The chemical affinities of oxygen and potassium are more apparent to us than are the chemical affinities of nitrogen, principally because they happen to possess very powerful affinities for some of the most prominent and abundant elements by which we are surrounded, whereas nitrogen possesses but feeble affinities for such elements but strong affinities for elements which happen not to be prominent or abundant in the laboratory. Nitrogen is doubly unfortunate in this respect, for *the elements for which it possesses the strongest affinity are elements which occur in the middle of cycles of the periodic system, and so are precisely those which happen to possess the power of self-combination most highly developed. This circumstance lowers the apparent stability of the compounds they produce with nitrogen in the way previously explained.*

It should be remembered that oxygen itself has only a feeble affinity for N, F, Cl, Br, I., &c., and were these the only common or prominent elements, we would consider O to be quite as inactive an element chemically as N appears to us under ordinary circumstances.

The compounds of O with Cl, for example, are characterised by their explosive properties, just as are so many nitrogen compounds.

Moreover, the nitrogen atoms themselves have a very considerable power of self-attraction, as is shown by the stability of the molecule N_2 in gaseous nitrogen, and by the occurrence of the diazo group —N=N— in organic chemistry, and this circumstance again lowers the apparent affinities of nitrogen for other elements in the way previously explained at length, for this attraction of nitrogen for itself has to be overcome before nitrogen will enter into combination with other elements.

On all these grounds, therefore, we must come to the conclusion that the current belief that nitrogen is an element characterised by its chemical inertness, and by the feebleness of its chemical affinities, is therefore hardly correct. *Nitrogen possesses chemical affinities of a strength almost comparable with those of chlorine or sodium, only it differs from these elements as regards the elements it exerts on them.*

ON SOME NEW RELATIONS OF ATOMIC WEIGHTS, AND TRANSFORMATIONS OF NEON AND HELIUM.

By Dr. HENRY WILDE, F.R.S.

At an extraordinary general meeting of the Manchester Literary and Philosophical Society, held on July 22nd, a paper was read by Dr. Henry Wilde, F.R.S., on "Some New Multiple Relations of the Atomic Weights of Elementary Substances, and on the Classification and Transformations of Neon and Helium." In several of the author's papers on the "Origin of Elementary Substances," published by the Society, 1878—1906 (see Chemical News, 1878, xxxviii., p. 66 *et seq.*), special attention was directed to the seventh series of his classification, on account of the magnitude and importance of its primary members in the economy of nature, viz., nitrogen, silicon, iron, and gold.

Silicon in combination with oxygen constitutes more than half the weight of the earth's crust, and is the principal constituent of glass for all the purposes of civilised life.

The arbitrary policy of several writers in doubling the atomic weights of four of the gaseous members of this series, viz., neon, argon, krypton, and xenon, induced the author to review the multiple relations of the seventh series with the important result (1) that six triads are formed out of the eight principal members of the series, in which the sum of the atomic weights of the extreme members is double the atomic weight of the means, and are all multiples of seven. Triads of atomic weights have been fully recognised by Dumas, Faraday, and other philosophical chemists, as indubitable evidence of community of origin, of transmutation, and important factors in the classification of elementary substances.

Radium (as was indicated in Dr. Wilde's tables of elements some years previous to its discovery) is one of the synthetic transformations of helium, and is the next higher member of the series of barium, as was since confirmed by Mme. Curie. Helium is also shown in the author's table of 1878, as the analytic transformation ultimate of radium and other members of the second series of elements.

The positions of helium and neon, as the transformation ultimates of the second and seventh series respectively, are further interesting in connection with the recent announcements that these elements have been found in glass vessels and tubes in which they had no previous existence. Assuming the reality of these observations, the phenomena not only admit of explication from Dr. Wilde's classifications, but also account for the discordant results obtained by the experimenters engaged in the research. One of the investigators could only find neon, while others, working independently, found helium alone, and in other cases a mixture of both gases. These results were of sufficient interest to induce the author to ascertain the composition of various glasses used in the arts.

The principal and most important constituent of the glasses tabulated by Dr. Wilde is silicon, the transformation ultimate of which is neon. The next important constituents of the glasses are barium, calcium, and lead; all members of the second series of elements, the transformation ultimate of which is helium. The alkali metals, sodium and potassium, are constituents of nearly all glasses, and their transformation ultimates (with others of the first series) will be hydrogen and neon, but without helium.

All the silicates of the first and second, and some of other series, are easily vitrified in small quantities in laboratory crucibles. Their spectra can then be examined during electrification in tubes (under suitable conditions of temperature and pressure) for the discovery of new elements, and the identification of those already known.

ANALYSIS OF FERRO-TITANIUM.

By A. R. SCOTT.

The following method for the determination of silicon, titanium, aluminium, iron, and manganese will be found very simple and accurate, especially so with regard to the complete separation of titanium and aluminium.

The method of estimating the aluminium by the long fusion with sodium carbonate, &c., is a long and tedious process, and the results obtained are not at all reliable.

Method.—Weigh out 0·25 grm. of the finely powdered alloy, and fuse with about 10 grms. of potassium bisulphate in a deep platinum basin. Fuse until no grit can be felt with a platinum rod. Cool, and put basin and contents into a porcelain evaporating basin. Extract with water, and add 10 cc. of concentrated H_2SO_4. Allow to stand on edge of hot plate for an hour. Filter into 600 cc. beaker. Wash with hot water, and ignite residue in platinum crucible. Fuse contents of crucible with a little potassium bisulphate, and extract as before with water and a few drops of H_2SO_4. Filter, and add filtrate to main filtrate. Ignite residue in a tared platinum crucible, cool and weigh. The increase in weight is SiO_2, with a little Fe_2O_3 and TiO_2. H.F. the residue, and weigh; the loss is SiO_2—calculate to silicon. Dissolve the residue in a little HCl; transfer to small beaker. Add NH_4OH, boil and filter; ignite in platinum crucible and weigh as

Fe_2O_3. Calculate to Fe. Any difference in the weight of residue after volatilisation of SiO_2 will be TiO_2; calculate to Ti.

Titanium.—Boil up combined filtrates from the SiO_2, and add ammonium hydrate until slight precipitate appears; clear with a few drops of hydrochloric acid, and add about 15 grms. sodium thiosulphate dissolved in water. Boil for fifteen minutes, and filter through pulp filter. Wash with acetic water. Transfer precipitate to tared platinum crucible, ignite strongly, and weigh as TiO_2. Calculate to Ti.

Iron and Aluminium.—Boil down the filtrate to fairly low bulk, and add about 200 cc. of hot water; boil down again. Continue the addition of water and the boiling until clear. Oxidise with bromine water, filter off any TiO_2 that may have got through the filter, and ignite same. Boil up the filtrate and add ammonium hydrate; filter into conical flask. Ignite the precipitate, and weigh as $Fe_2O_3+Al_2O_3$. Dissolve up the combined oxides in hydrochloric acid, reduce with stannous chloride, and titrate the Fe with potassium dichromate in the usual way. The difference after calculation will be *aluminium*.

Manganese.—To the cooled filtrate add bromine and ammonium hydrate, boil and filter. Ignite, and weigh as Mn_3O_4. Calculate to Mn.

Old Hall Road, Gatley.

PREPARATION OF THE NITRITES OF THE PRIMARY, SECONDARY, AND TERTIARY AMINES BY THE INTERACTION OF THE HYDROCHLORIDES OF THE BASES AND ALKALI NITRITES.

EXPLANATION OF THE ACTION OF NITROUS ACID ON THE AMINES.

(PART I.).

By PANCHANAN NEOGI, M.A., Senior Professor of Chemistry, Government College, Rajshahi, Bengal, India.

NEOGI and Adhicari (*Trans. Chem. Soc.*, 1911, xcix., 116) have already shown that ammonium nitrite can be prepared in fairly large quantities by subliming in a vacuum a concentrated solution of the mixture of ammonium chloride and alkali nitrites. Neogi (*Trans. Chem. Soc.*, 1912, ci., 1608) has also shown that coniinium nitrite may be prepared by distilling in a current of steam under reduced pressure a mixture of the hydrochloride and sodium or potassium nitrites. In continuation of the work referred to above, a systematic attempt has been made to prepare the amine nitrites by the interaction of the hydrochlorides of the bases and alkali nitrites. Experiments have abundantly shown that this method of preparing the amine nitrites is a general one. The success of the isolation of the amine nitrites from mixtures of the hydrochlorides of the bases and alkali nitrites lies on two facts hitherto unobserved:—

1. The amine nitrites may be distilled off in steam under reduced pressure in a very pure condition.

2. The amine nitrites, which are comparatively unstable in the solid or liquid condition as the case may be, are, in general, *stable in solution*, and, in fact, most of them may be concentrated to a small bulk on the water-bath without great loss.

The actual isolation of ammonium nitrite and a large number of amine nitrites affords ample confirmation of the theory already advanced by the author (Neogi, *Proc. Chem. Soc.*, 1911, xxvii., 242; *Trans. Chem. Soc.*, 1912, ci., 1610), that an amine nitrite is an intermediate compound in the well known interaction of amine hydrochlorides and sodium or potassium nitrite, or, in other words, amines and nitrous acid. The following equations show how the reactions really take place in two stages:—

(*a*) Ammonia or primary amine,—

$$R.NH_2+HNO_2=R.NH_2.HNO_2=R.OH+N_2+H_2O.$$

(*b*) Secondary amine,—

$$R_2NH+HNO_2=R_2NH.HNO_2=R_2N.NO+H_2O.$$

(*c*) Tertiary amine:—

$$1.\ R_3N+HNO_2 \rightleftharpoons R_3N.HNO_2.$$

$$2.\ 3R_3N.HNO_2=2R_3N+R_3NO_3+2NO+H_2O.$$

The nitrite is formed in each case at a low temperature, which decomposes at a higher temperature into the end-products of the respective reactions, viz., alcohol and nitrogen in the case of primary amines, nitroso-compound in the case of secondary amines, and the free amine in the case of the tertiary amines. In the case of the tertiary amines, however, the corresponding nitrates are also formed as a result of the decomposition of the nitrites.

This explanation does not, as a matter of course, apply to the purely aromatic amines which yield diazo-compounds.

Experimental.

The hydrochlorides of the amines were mostly indented from Kahlbaum, a few being obtained from E. Merck. They were found to be very pure, and were further purified from traces of ammonium chloride by exhausting them with small quantities of dry absolute alcohol, in which they were found to be almost wholly soluble. The general method of preparing the amine nitrites consists in vacuum distillation in steam. In the case of those nitrites, however, which sublime when heated in a vacuum, attempts were also made to isolate them by vacuum sublimation.

Sublimation in Vacuum.

One or 2 grms. of the hydrochloride were mixed with excess of sodium or potassium nitrite, and dissolved in a very small quantity (10 to 20 cc.) of water. The liquid was evaporated in a flask with a long neck, provided with a "catch" arrangement in order to avoid spirting, at 40° to 50° in the vacuum of the Töppler pump, and the gases evolved were collected in a Crum nitrometer. In order to drive off the last traces of moisture the entire neck of the flask was immersed in the bath. A capacious test-tube immersed in a beaker of cold water was inserted between the flask and the pump, which served as a condenser. The flask was held in a very slanting position so that particles of the liquid might not spirt into the neck of the flask. After the liquid was completely evaporated to dryness and traces of moisture had been driven off, the neck of the flask was partially raised, and the temperature of the bath was also gradually raised to the temperature at which the nitrite sublimed. When the experiment was completed the bottom of the flask was broken off, and the sublimed salt carefully washed out with water, mixed with the distillate contained in the test-tube, and the solution thus obtained was evaporated in a vacuum desiccator. The crystals were analysed by the "urea" and Crum-Frankland methods. As only small quantities of the hydrochloride were available the yield was not very satisfactory by this method. The success of the experiment will depend on the success with which the last traces of moisture have been driven off from the flask, as the nitrites are extremely hygroscopic.

Vacuum Sublimation in Steam.

A much better yield, however, of the nitrite was obtained by the process of vacuum distillation in steam. The operation was conducted in two ways:—(1) Distilling the solution in a current of steam whilst a vacuum was maintained, and (2) repeatedly distilling in a vacuum the mixture with fresh quantities of water. The first of these two processes has the advantage of being continuous, but the bumping is severe. The second process gives the better yield. The best results were obtained in the following manner:—The solution of the mixture was placed in a

distilling flask not less than 1 litre in capacity connected with a long condenser and receiver, which was in turn connected with a Geryk pump and manometer. The solution was diluted with water so as to fill not more than one-third of the flask, which was held in a very slanting position in order that the liquid might not spit into the neck of the flask. The flask was immersed in a capacious beaker containing water, which served as a bath. The distillation was conducted at a temperature suited to each case until the volume of the liquid was reduced to 30 to 50 cc. The flask was then thoroughly cooled, and the receiver detached. More water was added to the flask and a second distillate obtained. In this way several distillates were collected so long as they contained appreciable quantities of the nitrite. The total volume of the distillates with 1 or 2 grms. of the hydrochloride was between 300 to 500 cc. The nitrite, except in the case of ammonium nitrite, was wholly free from chloride. In this way 60 to 80 per cent and in some cases almost theoretical quantity of the nitrites, passed into the distillate, provided the temperature at which distillation was conducted was sufficiently low and the volume of the distillate sufficiently large.

In order to obtain the solid or liquid nitrite from the large volume of the distillate two methods were employed. In the case of those nitrites the solutions of which decompose to a large extent when heated on the water-bath, 100 cc. of the distillate was divided into four portions, each portion being kept in a vacuum desiccator. As the liquid in each diminished in quantity the four portions were mixed together and finally crystallised in one desiccator. In this way a good yield of the solid or liquid nitrite was obtained in three or four days. In the case of those nitrites the solutions of which do not decompose to a large extent when concentrated to a small bulk on the water-bath, the distillate was evaporated to a small bulk on the water-bath, and finally crystallised in a vacuum desiccator. Experiments show that the solutions of the great majority of the amine nitrites are fairly stable, and that they may be concentrated on the water-bath to a small bulk without great loss either by decomposition or volatilisation with steam at atmospheric pressure. The nitrites, as usual, were estimated by the "urea" and Crum-Frankland methods. Below are given results with each hydrochloride and sodium or potassium nitrite.

Interaction between Ammonium Chloride and Sodium or Potassium Nitrite. Steam Distillation in Vacuum.

Neogi and Adhicary (*Trans. Chem. Soc.*, 1911, xcix., 116) have already shown that pure ammonium nitrite may be prepared by first concentrating at about 50—60°, and then *subliming* at 80° a strong solution of this mixture.

It has been shown here that it can be prepared by steam distillation in vacuum also. The process as well as the apparatus employed have already been described before. One to 5 grms. of ammonium chloride were taken and mixed with excess of sodium or potassium nitrite. If the quantity of the distillate is large enough, almost quantitative yield of ammonium nitrite passes into the distillate, as will be seen from the following table. The temperature of the bath was maintained at 70°.

Wt. of NH_4Cl.		Vol. of distillate. Cc.	Wt. of $NH_4.NO_2$. Grms.
1 grm.	1st	210	0·63
	2nd . ..	140	0·32
	3rd	165	0·02
5 grms.	1st	122	1·00
	2nd . ..	106	0·77
	3rd	245	1·50
	4th	220	1·01
	5th	132	0·11

There was no nitrate in the distillate, as the "urea" nitrogen was equal to the nitric oxide by the Crum-Frankland method. Slight turbidity was produced by the addition of silver nitrate, thus showing that minute quantities of ammonium chloride pass into the distillate. The solid nitrite was obtained by concentrating 100 cc. of the first distillate in four vacuum desiccators, and freed from any ammonium chloride by means of absolute alcohol, in which it was almost wholly soluble. The operation took four days. The salt was white, slightly tinged greenish, extremely deliquescent, and very soluble in water and alcohol.

0·1160 gave 48·0 cc. N_2 at 30° and 755 mm. (made up to 10 cc. with water, of which 1 cc. = 4·8 cc. N_2), hence N ("nitritic") = 22·2 per cent. $NH_4.NO_2$ requires N (nitritic) = 21·8 per cent.

Attempts were also made to obtain the solid nitrite after concentrating the dilute distillate to a small bulk on the water-bath. 250 cc. of the distillate containing 1·36 grms. ammonium nitrite was concentrated on the water bath to 20 cc. It was found that the concentrated liquid still contained 54·3 per cent ammonium nitrite, the rest either decomposing into nitrogen and water or passing away with steam. The proportion of ammonium nitrate was small, as the ratio of the volumes of nitrogen and nitric oxide was 11·4 cc. + 11·8 cc. The crystals obtained in this way were more greenish in appearance and contained appreciable quantities of this nitrate. Thus this process might serve as a rapid method of obtaining not very pure samples of ammonium nitrite, the pure substance being obtained by crystallising without concentration on the water-bath.

As ammonium nitrite decomposes according to the equation $NH_4NO_2 = N_2 + 2H_2O$, the evolution of nitrogen by the action of ammonium chloride and sodium or potassium nitrite, or, in other words, of nitrous acid on ammonia, is simply the end-product of the reaction, the intermediate compound being ammonium nitrite.

The general similarity of the properties of ammonia and the primary amines, and particularly the similarity in the action of nitrous acid on ammonia and the primary amines, induces the author to regard ammonia as a primary amine. The name hydramine is suggested for ammonia, regarding it as a primary amine.

Benzylammonium Hydrochloride and Sodium or Potassium Nitrite. Sublimation in Vacuum.

One or 2 grms. of the hydrochloride purified from absolute alcohol (Cl = 23·8 per cent found, Cl = 24·7 per cent calc.) were taken, and the mixture of the hydrochloride and alkali nitrite was dissolved in a minimum quantity of water and transferred to the flask, and the Töppler set to work. The temperature of the bath was maintained between 40° and 50° during the evaporation of the water. Only very small quantities of nitrogen collected in the nitrometer, thus showing that very little action took place in solution. The entire neck of the flask was immersed in the bath, and when no more water remained in the flask, it was partially raised, and the temperature raised to 60°, when white crystals began to collect in the cooler parts of the neck of the flask, and at 60° to 70° a good quantity collected in white clusters of crystals. A small quantity of a gas collected in the nitrometer in the meantime, which was found to be nitrogen. On disconnecting the apparatus the sublimed salt was found to be pure benzylammonium nitrite containing no chloride. Blank experiments showed that in vacuum benzylammonium hydrochloride commenced to sublime at about 130°. The distillate contained in the test-tube also contained appreciable quantities of the nitrites free from chloride. The two solutions were mixed together, crystallised in a vacuum desiccator, and tested. The crystals were white, deliquescent, very soluble in water and alcohol.

If, however, the temperature was rapidly raised to 80° and above, the salt began to melt, and finally disappeared, and at the same time the evolution of gas was brisk. The gas on examination was found to be almost pure nitrogen, and the liquid in the test-tube an aqueous solution of benzyl alcohol, which was recognised by its smell and conversion into benzaldehyde on oxidation with nitric acid. The formation of benzyl alcohol and nitrogen is very

readily explained as the result of the decomposition of benzylammonium nitrite according to the equation (*cf.* Ray and Datta, *Trans. Chem. Soc.*, 1911, xcix., 1476) $C_6H_5.CH_2.NH_2.HNO_2 = C_6H_5.CH_2.OH + N_2 + H_2O$.

(To be continued).

THE SULPHOCYANATE-PERMANGANATE METHOD FOR COPPER IN ORES.

By D. J. DEMOREST.

Under the proper conditions copper may be precipitated practically completely as cuprous sulphocyanate. It is true that a qualitative test for copper may be obtained in the filtrate from the cuprous sulphocyanate when potassium ferrocyanide is added, but this is due to the presence of only about 0·0001 grm. of copper, as the writer has found by colorimetric measurements. Furthermore, the writer has found that practically all the copper added to the solution before precipitation may be recovered from the precipitate by electrolysis.

In Guess's method for copper the cuprous sulphocyanate is dissolved on the filter with sodium hydroxide, leaving the cuprous hydroxide on the filter while sodium sulphocyanate goes through. The filtrate is then made acid with sulphuric acid and is titrated with permanganate. Theoretically, the titration reaction is—

$$5HCNS + 6KMnO_4 + 4H_2SO_4 = 5HCN + 3K_2SO_4 + 6MnSO_4 + 4H_2O.$$

Practically, however, the oxidation in acid solution is never complete, and an empirical factor must be used amounting to about 5 per cent of the copper present, according to Guess's tables of correction given in Low's "Technical Methods of Ore Analysis." This is also in accord with the writer's experience and with that of Grossman and Hölter (Grossman and Hölter, *Chem. Ztg.*, xxxiii., 348).

It occurred to the writer that if the permanganate were added to the sulphocyanate in alkaline solution until about as much was added as would be required to titrate the sulphocyanate in acid solution, and if then the solution were made acid, the titration might be finished by a few drops, and in this way complete oxidation might be brought about and no empirical factor would be needed.

It is easy to tell when enough permanganate has been added to the alkaline solution by testing a drop or so on a white plate with a drop of an acid solution of ferric chloride. If not enough permanganate has been added a red colour develops, but if enough has been added no red appears. It is not necessary to run in permanganate until no red is obtained on testing. When the red colour of the test is very faint the solution may be made acid and the titration finished in the usual way.

Process of Analysis.

Weigh out enough of the ore to have from 0·05 grm. to 0·30 grm. of copper present. Transfer the sample to a 200 cc. beaker, add 5 cc. of strong hydrochloric acid and heat for several minutes; then add 10 cc. of nitric acid and digest on a hot plate until the oil is completely decomposed. Then add 10 cc. 1 : 1 sulphuric acid and boil down until fumes of SO_2 appear. Cool and add 50 cc. of water containing 3 grms. of tartaric acid and heat until all soluble salts are in solution. Cool and add ammonia until the solution turns a deep blue, then add sulphuric acid until the liquid becomes acid, then add 1 cc. more. Now add 1 grm. of sodium sulphite dissolved in 20 cc. of water, heat nearly to boiling, and add slowly and with vigorous stirring 1 grm. of potassium sulphocyanate dissolved in 20 cc. of water. Heat at a nearly boiling temperature for several minutes to coagulate the precipitate and dissolve out of it all tartaric acid. Cool somewhat and filter while still hot through, preferably, an asbestos mat on a Gooch filter. Wash well with water and rinse out the suction flask. Then pour through the crucible 30 cc. of a hot 10 per cent sodium hydroxide solution and wash well with water.

Warm the filtrate to about 50° and proceed to titrate. Run in slowly at first, while the flask is vigorously shaken, the standard permanganate solution. The solution in the flask turns green, due to the K_2MnO_4 formed. After about 10 cc. have been run in, take out a drop of the solution and place it in a drop of strong hydrochloric acid on a paraffined white plate; then add a drop of a 10 per cent solution of ferric chloride. If a red colour appears continue to add the permanganate solution, testing after each 5 cc. until the red becomes weak, then test more frequently until the red colour of a test becomes quite faint. Then add 30 cc. of 1 : 1 sulphuric acid and shake the flask until the MnO_2 all dissolves and finish the titration to the usual permanganate end point. This will require perhaps 1 cc. of permanganate.

Notes on the Process.

Fairly close results may be obtained by titrating carefully in the alkaline solution until five drops of the solution give no red colour with ferric chloride. But it is easier and more accurate to titrate only to an approximate end in the alkaline solution and finish in an acid solution. It is important that the precipitation be made as above directed with vigorous stirring and that the solution be digested on the hot plate after precipitation.

Under the conditions of titration the permanganate is reduced in the alkaline solution thus:— $2KMnO_4 = K_2MnO_4 + MnO_2 + 2O$. The oxygen possibly oxidises the sulphocyanate to tetrathionate, but of this the writer is not sure. He has proved by filtering off the MnO_2 and weighing it and by titrating the permanganate in the filtrate that the permanganate is reduced as above written. However, it makes no difference what reaction takes place in the oxidation of the sulphur in the alkaline solution, since the test for sulphocyanic acid is made on the plate in a strongly acid solution and the reaction between the sulphocyanate and the manganate and manganese dioxide completes itself there. The manganese dioxide does not settle out of the solution unless it stands a long time.

According to the titration reaction given in the second paragraph of this article 5 atoms of copper are equivalent to 6 molecules of $KMnO_4$ or 30 atoms of iron. Therefore, the iron value of the permanganate multiplied by Cu/6Fe or 0·1897 gives the copper value of the permanganate. The permanganate used by the writer equals 0·01 grm. Fe, or 0·001897 grm. Cu per cc.

After the filtrate has cooled, a crystalline compound of tartaric acid may separate. Hence the solution should be filtered hot.

The following are some results obtained by the above method:—

Copper.		Copper.	
Present.	Found.	Present.	Found.
0·1870	0·1890	0·0600	0·0596
0·1503	0·1511	0·0605	0·0603
0·1117	0·1125	0·1610	0·1630
0·1666	0·1668	0·0663	0·0667
0·0940	0·0930	0·1103	0·1109
0·2005	0·2017	0·1140	0·1147
0·2220	0·2224	0·1000	0·1001
0·2220	0·2210	0·1000	0·0999

The later results were the most accurate and were obtained after the necessity of digesting the precipitate in the hot solution was learned.

No elements interfere except, according to Low, silver. This is easily removed. If there is any lead present, the lead sulphate obtained after evaporating to fumes of SO_3 should be filtered off after the soluble salts are dissolved.—*Journal of Industrial and Engineering Chemistry*, v., No. 3.

REPORT ON THE ACTUAL STATE OF RUBBER ANALYSIS.*

By Prof. F. WILLY HINRICHSEN, Berlin.

In view of the great difficulties which the analyses of crude and of vulcanised rubber offer we should endeavour to agree upon the various methods of analysis, in order that similar tests conducted at different spots will lead to the same results. An international agreement upon this question would be particularly desirable.

I. *Analysis of Crude Rubber.*

The crude rubber contains, as is well known, in addition to the caoutchouc proper and to the mechanical impurities, such as sand, bark, &c., also moisture, mineral constituents, resins, and albuminoids. Of practical importance are above all the contents in pure rubber or caoutchouc, in mechanical admixtures, and in resins. The percentage of the latter affords a certain measure for the technical value of a kind of rubber, since the product is considered all the more valuable, the smaller its percentage in resins. The mechanical impurities are removed in the works by washing with water between rollers. The magnitude of the loss by washing is a second criterion for the applicability and the value of a commercial product. This washing loss is ascertained in the laboratory in a similar manner as in the works, by washing a sample of rubber on a small experimental roller. It is primarily essential for these experiments that the sample selected represent a fair average of the product.

As regards the chemical analysis of crude rubber, we should in the first instance determine whether the test is to be made with the original material or with the washed material. It would in general appear advisable always to make use of the washed material which has been air-dried.

The moisture is suitably determined in a specially weighed portion by drying *in vacuo* over sulphuric acid at gentle heat, until the weight remain constant.

For the determination of the resins 5 grms. of the finely-cut air-dried materials are completely extracted with acetone in a Soxhlet apparatus. Ten hours will in general be sufficient for this operation; the middle portion of the Soxhlet apparatus is suitably made of brown glass in order to prevent any action of the light on the material to be extracted. The dimensions of the apparatus to be used should be agreed upon, since any deviations from these dimensions would alone affect the values found for the percentages of the resins.

The further tests of the resins for optical activity and saponification which can be made according to Hinrichsen and Marcusson, permit under certain conditions to draw conclusions as to the botanical origin of the product.

Several processes have been suggested for the direct determination of pure caoutchouc; among these are the reaction with nitrous acid leading to the production of nitrosites, and the tetrabromide reaction. The recent scientific investigation of these two methods has led to the result that both these tests are unreliable. We are hence limited, as before, to an indirect analysis. For this we require, in addition to the already mentioned determination of moisture and to the extraction with acetone, in the first instance the estimation of the percentages of mineral constituents and of albuminoids. The former can as a rule be deduced from the determination of the ashes. An approximate measure for the proportion of albuminoids present is afforded by the determination of the nitrogen percentage which is suitably effected by the method of Kjeldahl. By multiplying the resulting figure by 6·25, corresponding to a content of from 15 to 18 per cent of nitrogen in the albuminoid, the amount of albuminoids in the sample is approximately deduced. The difference between the component percentages of the impurities and 100 yields the percentage of pure caoutchouc in the material.

II. *Analysis of Vulcanised Rubber.*

The compositions of the various vulcanite rubber articles are so very manifold that a generally available method of analysis cannot be suggested. In many cases the constitution of the mixture cannot even approximately be ascertained by chemical means. When it is required to fix the conditions of supply for rubber materials, whose chemical composition is to be prescribed and to be controlled, we have for the present to bear the imperfection of our methods of rubber analysis in mind. Starting from this point of view the united German cable manufacturers have, for instance, prescribed for the standard leads a rubber mixture, which contains nothing but constituents that can be determined analytically with a certain degree of reliability, namely, in addition to rubber and to sulphur only inorganic additions and hydrocarbons of the paraffin series (ceresin).

Since the methods for the direct determination of pure caoutchouc (nitrosite, bromide, &c.) are still less applicable to vucanised products than they are to the raw material, we have to have recourse to the indirect analysis. In many cases the following mode of procedure will be satisfactory, especially when pitch, tar, asphalt, and similar materials are absent.

Five grms. of the sample are extracted with acetone in the same way as we described above for crude rubber. This process will dissolve, in addition to the resins originally present in the rubber and to any foreign resins possibly added, the free sulphur, further oils, hydrocarbons of the paraffins, and wax. The sulphur is determined in a special sample in the residue, which remains after evaporating the acetone solution, after oxidation with strong nitric acid to which a little free bromine should be added. Solid hydrocarbons are approximately estimated by taking up the residue of the acetone solution with alcohol and by precipitating from this solution the hydrocarbons by continued cooling down to $-5°$ C. When oils and foreign resins are present, an exact determination of the original rubber resin is not possible. The saponification figure does not constitute any measure for the amount of the additions, since some of the original rubber resins are themselves quite incapable of undergoing saponification, while parts of them may be highly saponifiable; it depends upon the origin of the material. When in addition to these resins only free sulphur and paraffin hydrocarbons are present, the resins may approximately be estimated by difference.

The material extracted with acetone is heated with hydrocarbons of high boiling point, for instance, petroleum or oil of paraffin, for the purpose of estimating the inorganic additions; these chemicals dissolve vulcanised rubber. The mineral additions (fillers) are, if possible, removed by filtration, if not, by centrifugation of the solutions which have been precipitated with benzine and have been washed with other organic solvents.

Another portion of the material which has been extracted with acetone is boiled for four hours under application of a reflux condenser with semi-normal alcoholic soda lye. The lye will saponify the usual technical factices. After filtering off the unchanged material, water is added to the solution; by addition of mineral acids the factice-acids are then precipitated, taken up with ether and determined. Any conclusion as to the percentage of the originally added factice is unsafe for this reason already, that the different kinds of commercial factices contain very strongly varying proportions of constituents soluble in acetone.

When we want to deduce the amount of pure caoutchouc in the mixture, we need now only proceed to the estimation of the bound sulphur. For this purpose we determine the total amount of sulphur in the mixture and we deduct from this the free sulphur, the sulphur which is incor-

* Paper presented at the Sixth Congress of the International Association for Testing Materials, New York. From *Chemical Engineer*, xvii., No. 4.

ganically bound, and the sulphur which is contained in the factice-acids.

The determination of the total sulphur is simplest and safest carried out by the other process, oxidation with nitric acid and with magnesium nitrate in a spherical flask, or by the Hinrichsen process, electrolytic oxidation in nitric acid. The sulphur which was bound by inorganic compounds is directly estimated in the filling materials, and the factice-sulphur is found in analysis of the factice-acids.

If we further know the moisture and the nitrogen (albuminoid) contents of the samples, the difference will give us approximately the percentage of pure caoutchouc.

When the mixture contains, in addition to the in gredients above specified, also tar, pitch, asphalt, or similar materials, any reliable analysis of the product may be regarded as out of question. Extraction by means of pyridin has formerly been proposed; it is inapplicable, however, since the pyridin also dissolves some rubber.

THE ELECTRODEPOSITION OF TIN.*

By EDWARD F. KERN.

This paper is a compilation of data collected from all the available literature and contributed to the Symposium on the Electrodeposition of Metals, in accordance with the request of the President of the Society.

Tin is largely used as a protective coating to articles of iron, steel, copper, brass, and bronze. The process of coating large articles of iron, steel, and copper by merely bringing their cleaned surfaces in contact with molten tin and then removing the excess either by means of rolls or by centrifugal machines, is so much cheaper than electrolytic methods, and moreover gives such sound and perfect coatings, that the electrodeposition methods have found little application except for coating small articles and those which have an irregular surface.

A great amount of electrodeposition of tin is done for the coating of small articles such as pins, hooks, eyes, screws, clasps, &c., for which purpose this method is preferable. Another application of electrodeposition is that of giving a preliminary coating to iron or steel, which is subsequently to receive an electrodeposit of a metal which is more electropositive than iron.

The consideration of electrolytes, as given below, was done in the following order under each of the headings:—A—Acid Electrolytes, B—Neutral Electrolytes, C—Alkaline Electrolytes.

I. *Electrodeposition of Tin by Immersion.*

The use of the immersion process of tinning is principally for coating small articles of copper, brass, and iron, such as hooks, eyes, pins, buttons, clasps, screws, &c., with a thin bright adherent deposit of tin. The immersion method consists in placing the articles in contact with either metallic tin or zinc in a boiling solution of a tin salt or a solution containing a tin salt and one or more salts.

1. One of the most generally used immersion baths is a saturated solution of cream of tartar (potassium hydrogen tartrate) to which has been added from 15 to 30 grms. of tin chloride per litre. Boil and place the articles in the boiling solution, and stir with a rod of metallic tin (Barclay and Hainsworth, "Electroplating," 1912 Ed., p. 333; Fields, "Principles of Electroplating," 1912 Ed., p. 221). Instead of using a rod of tin to stir the solution the articles may be placed in alternate layers with granulated or sheet tin, which will cause the articles to be coated with a white smooth adherent deposit of tin (Fields, "Principles of Electroplating," 1912 Ed., p. 211). If the metallic tin be replaced by metallic zinc, and stannous chloride added to the solution from time to time, thicker deposits of tin on the articles may be obtained and in a shorter time. In this case no tin is being added to the solution to replace that which is deposited on the articles, so it will be necessary to reject the solution when much zinc has accumulated in it (Fields, "Principles of Electroplating," 1912 Ed., p. 211; Barclay and Hainsworth, "Electroplating," 1912 Ed., p. 333; "Metal Industry," 1906, iv., 225). The articles, after proper coating has been obtained, should be rinsed in water, dried by shaking with sawdust, and polished with a scratch brush or by rolling in a polishing barrel.

2. An immersion solution which has given satisfaction for coating iron and steel articles with tin was used by Roseleur. It is prepared by dissolving 20 to 30 grms. of ammonium alum and 1 to 2 grms. of anhydrous tin chloride per litre of water (Barclay and Hainsworth, "Electroplating," 1912 Ed., p. 333; *Brass World*, 1912, viii., 180). Potash alum does not give good results. Fused tin chloride is used because it does not contain any free acid which will cause the coating to peel. The solution must be used boiling, and the iron articles must be clean of rust and grease, which are removed by an "alkali dip" and by a pickling solution. A bright coating of tin will be produced within thirty to sixty seconds. The solution must be replenished with tin from time to time by adding fused tin chloride in the original proportion to the volume of solution. As iron stands above tin in the E.M.F. series, the iron replaces an equivalent of tin in the solution, so when iron has accumulated to an amount which causes the coating to deposit in non-adherent form the solution must be rejected.

3. The solution devised by Elsner for coating copper and brass articles, and which gives reliable results (Barclay and Hainsworth, "Electroplating," 1912 Ed., p. 333) is prepared by dissolving 2 grains of sodium chloride and 2 grains of stannous chloride in 1 litre of water. It is used in the same manner as solution 1.

II. *Electrolytic Determination of Tin.*

Tin may be quantitatively precipitated from certain solutions by electrolysing them under such conditions of temperature, composition, or solution, and current density as have been found to give accurate results. The solutions which give the most satisfactory results are in most cases those which contain the tin either as ammonium sulphostannate.

1. Smith states that tin may be quantitatively deposited from a solution which contains ammonium oxalate (Smith's "Electro-analyses," 1911 Ed., p. 169; Neumann-Kershaw, "Electrolytic Methods of Analysis," 1898 Ed., p. 149). Potassium oxalate is not advisable, as a basic salt of tin is liable to separate upon the anode. The conditions which were found to give good results are:—The solution, 125 to 150 cc. in volume, containing about 0·5 grm. of tin as chloride and about 4 grms. of ammonium oxalate, is acidified with 9 to 10 grms. of oxalic acid (acetic acid may be used instead of oxalic acid), heated to about 65° C. and electrolysed at C.D. of 1 to 1·5 ampère per sq. decimetre. Deposits formed under these conditions are bright and adherent.

2. Classen found that dense bright adherent deposits could be quantitatively formed in an acid ammonium oxalate solution. He added 120 cc. of a saturated solution of ammonium oxalate to 25 cc. solution containing 0·9 to 1·0 grm. of stannic ammonium chloride, then electrolysed at 30° to 35° C. with current of 0·3 to 0·6 ampère and voltage at 2·8 to 3·8. Acid ammonium oxalate must be added at intervals if a larger quantity of tin is to be deposited. Time required was about nine hours for complete precipitation. The tin separated as a brilliant white adherent deposit. It was washed, dried, and weighed in usual way (Smith's "Electro-analysis," 1911 Ed., p. 169;

* Paper presented at the Twenty-third General Meeting of the American Electrochemical Society, at Atlantic City, N.J., April, 1913. From the *Chemical Engineer*, xvii. No. 6.

Neumann-Kershaw, "Electric Methods of Analysis," 1898 Ed., p. 149).

In case the tin is to be determined in a solution containing it as potassium sulpho-stannate, Classen recommends that it be converted into the oxalate, and then electrolysed. This is accomplished by acidifying the solution with hydrochloric acid, then boiling off the hydrogen sulphide, and adding hydrogen peroxide to oxidise the tin to metastannic acid, which is a white precipitate. Add a few cc. of sulphuric acid, neutralise with ammonia, and again add hydrogen peroxide. Filter out the metastannic acid, wash, dissolve in a solution of oxalic acid and ammonium oxalate, and electrolyse under conditions given above. Use ordinary platinum electrodes.

3. C. Engel gave the following conditions for quantitatively depositing tin by electrolysis as a bright white smooth adherent deposit:—Add to the solution, containing about 1 grm. of tin as ammonium stannic chloride, a few cc. of oxalic acid solution to clear the turbidity, then add 0·3 to 0·5 grm. of hydroxylamine hydrochloride or sulphate, 2 grms. ammonium acetate, and 2 grms. tartaric acid. Dilute to 150 cc., heat to 60° to 70° C., and electrolyse at C.D. of 0·9 to 1 ampère per sq. dm. and potential of 4 to 5 volts (*Journ. Soc. Chem. Ind.*, xv., 219; Neumann-Kershaw, "Electrolytic Methods of Analysis," 1898 Ed., p. 151; Smith's "Electro-analysis," 1911 Ed., p. 171).

4. Campbell and Champion determined tin in ores by fusing 1·0 grm. of the finely ground sample with 5 to 6 grms. of a mixture of equal parts of sodium hydroxide and sulphur for one and a-half hours at red-heat in a porcelain crucible. The fusion was then digested with 40 to 50 cc. of hot water, the solution filtered, and the residue washed and discarded. The filtrate was acidified with hydrochloric acid, which precipitated the tin as stannic sulphide, boiled off the hydrogen sulphide, added 10 cc. concentrated hydrochloric acid, and gradually introduced 2 to 3 grms. of sodium peroxide until a clear solution was obtained. Boiled about three minutes, then filtered out the separated sulphur and washed. Added ammonia to the filtrate to permanent precipitation, and then 50 cc. of a 10 per cent acid ammonium oxalate solution. Electrolysed over night at C.D. of 0·1 ampère per sq. dm. and about 4 volts. Deposit of light colour and very adherent (Neumann-Kershaw, "Electrolytic Methods of Analysis," 1898 Ed., p. 150).

In the course of any analysis, when tin is obtained as sulphide, the electrolytic determination may be conducted by getting the precipitate into solution as chloride by digesting it at boiling with 10 cc. of concentrated hydrochloric acid and 70 cc. of water, to which is gradually added 2 to 3 grms. of sodium peroxide. Then proceed in the same manner as given above (*Journ. Soc. Chem. Ind.*, xvii., 1073).

5. Pasztor rapidly and quantitatively deposited tin from tartaric acid solutions which contained from 4 to 6 grms. of tartaric acid, 2 to 6 grms. of ammonium acetate, and 1 to 1½ grms. of hydroxylamine hydrochloride or sulphate per 150 cc. volume, electrolysed at 60° to 80° C. at C.D. of 0·8 to 1 ampère per sq. dm.

Pasztor also stated that stannous sulphide dissolved in hot hydrochloric acid solution containing ammonium chloride gave a clear solution from which the tin was quantitatively deposited (*Electrochem. Zeit.*, xvi., 281; Smith's "Electroanalysis," 1911 Ed., p. 171; Neumann-Kershaw, "Electrolytic Methods of Analysis," 1898 Ed., p. 151; Arrhenius, "Text-book of Electro-chemistry," p. 274).

6. Classen discovered that a dilute solution of tin containing an excess of ammonium sulphide would yield a quantitative deposit of the metal, but that the deposits formed in a sodium or potassium sulphide solution were dark grey and non-adherent (Smith's "Electro-analysis," 1911 Ed., p. 170; Neumann-Kershaw, "Electrolytic Methods of Analysis," 1898 Ed., p. 150). The conditions for obtaining a satisfactory deposit of tin from ammonium sulphide solution containing the tin as ammonium sulphostannate are:—150 cc. solution containing an excess of ammonium sulphide, heated at 50° to 60° C., and electrolysed at C.D. of 1 to 1½ ampère per sq. dm. and potential of 4 to 5 volts (Arrhenius, "Text-book of Electrochemistry," p. 274).

Use of Rotating Electrodes.—The use of rotating anodes, revolved at 300 to 500 times per minute, enables the quantitative precipitation of tin to be made from ammonium oxalate solutions and ammonium sulphide solutions in twenty to thirty minutes, giving a deposit like polished silver. The electrolysis is conducted with C.D. of 5 to 8 ampères per sq. dm. and E.M.F. of 5 to 8 volts (Smith's "Electro-analysis," 1911 Ed., p. 172).

Removal of Tin Deposits from the Cathode.—The deposit of tin on the platinum cathode may be readily removed by fusing with potassium bisulphate, or dissolving in a mixture of nitric acid and oxalic acid, or by means of dilute hydrochloric acid with a piece of metallic zinc in contact with the cathode (Smith's "Electro-analysis," 1911 Ed., p. 169).

III. *Electrodeposition of Tin by Separate Current.*

On account of the whiteness of tin and it not becoming tarnished by exposure to the atmosphere, an electrolytic deposit of this metal is much desired. There are many uses which could be made of small metallic articles which are coated with an adherent smooth dense bright deposit of tin, but the difficulty of obtaining such a deposit has hindered the larger practice of electroplating with tin.

A number of electrolytes have been suggested, some of which have been patented, but the choice of the proper solution for the coating of articles of iron, steel, copper, brass, or bronze will in most cases largely depend upon the character of the work to be done and the available conditions, such as the source and quantity of current, means of controlling the temperature of the electrolyte, size of the articles, and the method of handling and treating them before and after the electrolysis has been conducted.

The electrolytes which are given below are those which have been recommended and used for electroplating of tin. In many cases the published composition of the electrolytes was given in either ounces or pounds of the ingredients per gallon, but in order to allow ease of comparison of the different solutions, their compositions were calculated into grms. per litre, and temperatures were changed from Fahrenheit into Centigrade.

1. Good deposits of tin may be produced by using an electrolyte containing stannous chloride and acid ammonium oxalate. One litre of this solution is prepared by dissolving 25 to 30 grms. of crystallised stannous chloride in about 400 cc. of water, 55 to 65 grms. of ammonium oxalate, and 3 to 4 grms. of oxalic acid in about 400 cc. of water. Add the oxalate solution to the tin solution with vigorous stirring, so that the white precipitate which forms at first will dissolve. Dilute 1 litre and boil a few minutes. The deposits formed from this electrolyte are said to be excellent, and, further, the anodes corrode normally, so there is no need of adding tin salt to the electrolyte from time to time. This solution has the advantage that it can be mixed with a similarly prepared copper solution, and the mixed solution used for depositing a coating of bronze (Barclay and Hainsworth, "Electroplating," 1912 Ed., p. 331; Field's "Principles of Electroplating," 1911 Ed., p. 213).

2. Roseleur's tin bath is recommended as giving the most satisfactory deposits of any of the generally used electrolytes. It is prepared by dissolving 10 to 12·5 grms. of sodium pyrophosphate in 1 litre of water and suspending 1 to 1·5 grm. of fused stannous chloride in the solution by placing it in a copper screen or in a linen bag. Agitate till all the tin chloride is dissolved. The solution is at first cloudy, but finally becomes clear and is ready for use. Voltage required from 1·5 to 4 volts. Use pure tin anodes.

It is stated that any metal may be coated with tin in this solution, the deposit having a dead white lustre resembling silver, which may be polished by either scratch-

brushing or by burnishing. Articles of zinc, copper, brass, and bronze may be directly tinned in this bath, but those of iron and steel must be first tinned in an immersion solution (see I., 2) or else electro-coppered, then scratch-brushed, and finally placed in the tin bath (McMillian-Cooper, "Electrometallurgy," 1910 Ed., p. 248; Barclay and Hainsworth, "Electroplating," 1912 Ed., p. 331; Watt and Philip, "Electroplating and Electrorefining," 1911 Ed., p. 344; Langbein-Brannt, "Electrodeposition of Metals," 1909 Ed., p. 439).

The Roseleur electrolyte is the one most generally used for electro-tinning. It is capable of giving the whitest deposit of any of the tinning baths which are in general use. The objections to it are that it must be worked hot, that heavy deposits cannot be obtained except after a period of several hours, and that the anodes do not dissolve normally, which necessitates that a concentrated solution of tin chloride be added to the working solution from time to time.

The Roseleur bath has been modified in concentration by other electroplaters:—Weiss used a solution containing 1 grm. of fused stannous chloride and 5 grms. of sodium pyrophosphate per litre (McMillian-Cooper, "Electrometallurgy," 1910 Ed., p. 249). A solution recommended as giving excellent results is prepared by dissolving 15 grms. of sodium phosphate crystals in 1 litre of water, and adding 7·5 grms. tin chloride. Work at low current density (*Metal Industry*, 1906, iv., 138). Another solution, said to have been recommended by eminent authorities, contains 37 grms. sodium phosphate crystals and 20 grms. fused tin chloride per litre. The tension required for this electrolyte was given as 1 to 1·5 volt, when worked hot (*Metal Industry*, 1907, v., 376).

3. An electrolyte which gives good results when electrolysed at ordinary temperature is prepared by dissolving 15 grms. of ammonium chloride and 30 grms. of fused stannous chloride in a litre of water. Use pure tin anodes, and regulate the current so as to avoid pulverulent deposits (*Metal Industry*, 1911, ix., 519).

4. An electrolyte which is strongly recommended as giving excellent results is prepared by dissolving 45 grms. of diammonium stannic chloride per litre of water. Electrolyse at tension of about 1·5 volt (*Metal Industry*, 1907, v., 376).

5. A good lustrous deposit of tin may be produced by using an electrolyte prepared by dissolving 30 to 60 grms. of cream of tartar (potassium hydrogen tartrate) in a litre of water, and adding 7·5 to 15 grms. of tin chloride crystals. Use pure tin anodes, and electrolyse at temperature not less than 70° C. at E.M.F. of 3 to 5 volts. A good lustrous deposit can be obtained in twenty to thirty minutes; scratch-brush with a soft steel brush, or polish on a soft buff wheel, using Vienna lime and kerosene. Keep the solution between 5° and 6° B. (*Metal Industry*, 1908, vi., 162, 227; 1909, vii., 227).

6. A solution which has been used considerably for tinning articles of iron, steel, and brass is prepared by dissolving 60 grms. of caustic soda in about 800 cc. of water, and 22·5 grms. of fused stannous chloride in small amount of water, then pour the tin solution into the caustic solution and dilute to 1 litre. Electrolyse cold, using pure tin anodes, and potential of 1 to 1·5 volt (Bedell's ("Practical Electroplating," 1909 Ed., p. 143). If the solution becomes impoverished in tin it should be revived by adding fused stannous chloride. If solution assumes a milky appearance, add caustic soda until it clears. Keep at about 11° B.

While the work is being plated it takes on a frosty appearance which is usually porous; the work should then be removed from the bath and scratch-brushed. This may have to be repeated several times, if thick deposits are desired. When mechanical plating-barrels are used scratch-brushing will not be necessary, as the rolling and the rubbing of the articles cause them to become burnished. Articles of iron and steel must first be given a slight coating of copper in a copper cyanide electrolyte, preferably hot.

7. A tin bath which has given satisfaction is prepared by dissolving 12 grms. of metallic tin in hydrochloric acid, evaporating to expel the free acid, then adding to a solution of 25 grms. of potassium hydroxide, and diluting to 1 litre. The addition of stannous chloride must be made from time to time as needed (Barclay and Hainsworth, "Electroplating," 1912 Ed., p. 330).

8. Elsner used an alkaline electrolyte which he recommends as having given satisfaction for electro-tinning iron and steel. It was prepared by adding 25 grms. of tin tetrachloride to 1000 cc. of water and adding sufficient caustic potash to give a clear solution. He used cast tin anodes, and required a potential of 3 to 5 volts (McMillian-Cooper, "Electrometallurgy," 1910 Ed., p. 248).

9. Hearn prepared an electrolyte which he used for general work by dissolving 21 grms. of tartaric acid and 30 grms. of caustic soda in 1 litre of water, then adding 3 grms. of fused tin bichloride (McMillian Cooper, "Electrometallurgy," 1910 Ed., p. 249).

(To be continued).

THE SCIENTIFIC WEEK.

(From Our Paris Correspondent).

The Aroma of Coffee.

The tonic and stimulating properties of coffee have been known for a long time. Learned men attribute all the virtues of this precious produce to caffeine. But M. Gabriel Bertrand, of the Pasteur Institute, after a certain number of researches undertaken in collaboration with M. Weisweiller, has just discovered that an infusion of coffee owes it aroma, not only to caffeine, which has been studied for a long time past, but also to the presence of a volatile alkaloid recognised by chemists as being *pyridine*, the smell of which, however, in the mass, is disagreeable. It is probable that the infusion of coffee owes a part of its physiological action to pyridine, of which it contains a proportion corresponding to a quarter of a grm. per kilogrm. of coffee.

M. Gabriel Bertrand has observed that by adding caffeine to boiling sugared water, the aroma of coffee is obtained, but if to this decoction some pyridine is added, in a proportion equal to that which is normally contained in coffee, the aroma of the coffee immediately becomes much stronger. It would seem then that traces of pyridine increase the aroma of coffee.

Different varieties of coffee contain variable proportions of pyridine. The quantity of pyridine contained in a kilogrm. of coffee varies from 200 milligrms. to 250 milligrms.

The Presence of Boron in Milk and in Eggs.

The researches that Messrs. Gabriel Bertrand and H. Agulhon, of the Pasteur Institute, have already published concerning the presence of boron in the human organism, have demonstrated that, contrary to what had been sustained formerly, not only this metalloid exists in the animal organism as well as in vegetables, but moreover there is every reason to suppose and admit its normal presence in every degree of the zoological scale.

Following on these results, the same authors have come to think that boron may perhaps be a fundamental element of the living cellule, if, like iron and magnesia, it plays an indispensable part in nutrition exchanges. This question has led them to complete their statical researches by the examination of milk and of birds' eggs. The fact is there is some reason to suppose that if boron really possesses a cellulary importance, it must already exist in the first stages of life; that it must consequently exist in milk—that liquid that has to supply in itself alone, for a considerable period, all the alimentary requirements of the young mammifer. Likewise, boron must also be found in eggs, that is to say in a state of development, in which it is not necessary to take into considera-

tion the contamination of the organism by exterior contributions.

Now, concerning four species of milk (woman's, ass's, goat's, cow's) collected in the presence of the above-named authors, into vessels cleaned by them, the immediate research for boron each time gave them distinct results.

They have likewise discovered the presence of boron in birds' eggs. So, they conclude, that in all probability boron is to be classed along with other catalytic elements of the living cell.

THE SUBTERRANEOUS WATERS OF EGYPT.

Dr. Roux, the Director of the Pasteur Institute, has lately communicated to the Academy of Sciences a very interesting work of M. Audebean Bey, concerning the subterraneous waters of Egypt. This study gives a classification of the grounds from the point of view of their permeability.

The Chief Engineer of the Egyptian State Domains explains the differences that are remarked in the permeability of the soil in the valley of the Nile, by the deposits of various sorts, due to the divagations of the sinuosities of the branches of the river and of the natural canals during the pleistocene period, and by the changes effected in the dykes and the breaches of the ancient inundation basins in the course of the centuries during which lasted the system of submersion of flooding, &c.

M. Audebean Bey shows that with the works of mechanical draining, which are at present being undertaken in the North of Delta, it will be possible to give to the soil in that region, to-day waste and uncultivated, the fertility it possessed during the Grecian-Roman period, and perhaps even that of the most remote times. He adds also that when the time has arrived, it will be easy to drain and dry the lakes that lie along the Mediterranean coast and to cultivate the vast superficies they occupy.

THE PRESENCE OF RARE METALS IN MINERAL WATERS.

M. Jacques Bardet has made a whole series of researches concerning the presence of metals in mineral waters. These experiments, made by means of a spectrograph, have led the author to discover in mineral waters the presence of a large number of metallic elements that were entirely unsuspected; amongst others that are very frequent, that of germanium and of gallium, bodies the existence of which had up till now only been remarked in very rare minerals.

MISCELLANEOUS.

American Chemical Society.—*Rochester Meeting.*—The forty-eighth annual meeting of the American Chemical Society will be held in Rochester, New York, September 9th to 14th, inclusive. A meeting of the Council will be held on Monday night, September 8th, at the Hotel Seneca, immediately following a complimentary dinner to be given to the Council at seven o'clock. The programme will open with a general meeting on Tuesday at 10 a.m., in the Assembly Hall at Kodak Park. Members should make a special effort to be present at this opening meeting, as it will not only be one of the most interesting meetings of the session, owing to the fact that it will contain the general addresses, but the whole day will be one of special features, inasmuch as the members of the Society are to be the guests of the Eastman Kodak Company at luncheon following the morning meeting, and the afternoon will be spent in visiting their immense plant at Kodak Park. As the Eastman Company is making special efforts to entertain the membership, it is hoped that every member will endeavour to be present at this first session. A smoker will be held at 8.30 p.m., Tuesday, in Masonic Hall. The divisional meetings on Wednesday, all day, and Thursday and Friday mornings, will be held in the Eastman Building, University of Rochester. The President's address will be given at the East High School, Rochester, at 8 p.m., Wednesday; and the subscription banquet, Thursday night, at 7 p.m., at Powers Hotel. On Thursday and Friday afternoons, excursions will be open to the following manufacturing plants:—Bausch and Lomb Optical Co., Taylor Instrument Co., Curtice Bros. Co., J. Hungerford Smith Co., Moerlback Brewery, German-American Button Co., Genessee Reduction Co., Municipal Incinerator, Stecker Lithographic Co., and possibly others. The only opportunity to visit the Eastman Kodak Company will be on Tuesday afternoon. There are already signs that the meeting this September will be the largest that the Society has ever held as a separate organisation, and it is probable that from 700 to 1000 chemists will be present. All papers for the meeting must be in the Secretary's hands on or before August 22nd, or in the hands of secretaries of divisions by August 20th, in order to be on the programme; especially the secretary of the Organic Division requests that organic papers be sent direct to him.

Institute of Chemistry.—*Pass List: June—July* (1913) *Examinations.*—Of thirty-three candidates who presented themselves for the Intermediate Examination, sixteen passed:—R. L. Amoore, R. O. Bishop, A. Dingwall, J. W. Donaldson, B.Sc. (Edin.), J. G. Duncan, A. Dunsmore, J. S. Frith, Peter Kerr, B.Sc. (Edin.), K. G. Lochhead, J. W. Lorimer, H. V. Parker, B.A. (Cantab.), H. C. Reynard, F. Smith, F. W. Snelgrove, B.Sc. (Lond.), A. R. Steele, and A. F. Weiss, B.Sc. (Lond.). Of forty-five candidates who presented themselves for the Final Examination, twenty-four passed. In the Branch of Mineral Chemistry:—B. Campbell, B.Sc. (Lond.), J. A. Pickard, B.Sc. (Lond.), A.R.C.S. (Lond.), E. A. Rayner, B.Sc. (Lond.), and E. W. Skelton, B.Sc. (Lond.); in the Branch of Metallurgical Chemistry: R. J. Dunn, B.Sc. (Birm.); in the Branch of Physical Chemistry: (Miss) G. Thompson, B.Sc. (Lond.); in the Branch of Organic Chemistry: J. S. Bainbridge, B.Sc. (Leeds), A. L. R. Clarke, B.Sc. (Lond.), A. Cunningham, B. B. Dey, M.Sc. (Calcutta), J. R. Gray, G. N. Grinling, E. S. Hawkins, B.Sc. (Birm.), P. C. R. Kingscott, A.R.C.S. (Lond.), D. E. Sharp, B.Sc. (Aberdeen), T. F. Smeaton, E. W. Smith, B.Sc. (Lond.), and R. Wheatley, B.Sc. (Leeds); in the Branch of the Chemistry of Food and Drugs, and of Water: (Miss) D. J. Bartlett, H. B. Brown, D. W. Kent-Jones, B.Sc. (Lond.), H. A. Phillips, H. V. Potter, and S. H. Stroud.

Growth of Sponge in Filtering Beds of Waterworks.—An interesting scientific announcement was made recently at a meeting of the Cardiff Waterworks Committee, when the Waterworks Engineer, Mr. C. H. Priestly, said that he, in conjunction with Professor Parker, had succeeded in overcoming the difficulty experienced with regard to the growth of sponge in the pipes in the filtering area at the Llanishen reservoir. The agent employed was a solution of common salt, and so successful had it proved that up to the present week there was no sign of the reappearance of the growth. Mr. Priestly added that Professor Parker himself was so impressed with the result of the experiment that he proposed writing a paper on it to the Geological Society, as a record might prove of assistance to other waterworks encountering similar trouble. The Chairman (Ald. C. H. Bird) said it was very satisfactory to learn that this trouble had at length been got over.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

New Copper Alloy—We notice in CHEMICAL NEWS, vol. cvii., p. 283, an extract relating to a new copper alloy. Can you inform us how we can obtain samples containing varying proportions of the cobalt-tin alloy? We desire to make some tests with this acid resisting metal.—J. and W. KEARNS.

THE CHEMICAL NEWS.

VOL. CVIII., No. 2802.

NOTES ON PLANT CHEMISTRY.

By Dr. P. Q. KEEGAN.

The Bitter Principles.

THESE principles of plants are neutral, indifferent, and proximate, and have indistinctly marked chemical characters; they seem mostly to be decomposed glucosides of a certain kind, but a few are really lactones. In all cases they arise as direct or indirect products of deassimilation. According to Russell (*Comptes Rendus*, 1904, cxxxix.), the glucosides of the underground parts of plants disappear in spring, and may be present in the stems and leaves only at certain periods, being absent in the adult organs; in some cases they pass over entirely into the central portions of the stem or leaf, while in the flowers they eventually migrate into the seeds. It would seem that these special movements of glucosides are attended by very important chemical transformations which hitherto have been ignored by investigators, the subject of the origin of the bitter principles not receiving that attention which it merits. The ordinary conception of a glucoside is that it is a combination of sugar with an aromatic residue of some kind, but to me it seems difficult to believe that this sugar has at any time been produced independently, and afterwards become combined with a foreign body.

It is much more probable that a hydrolytic scission occurs, with the simultaneous formation of a reducing matter simply derived from the molecule of the glucoside itself, and not necessarily a carbohydrate. However, if we consider the order Labiatæ, we find that while glucosides are rare therein, bitter principles abound in varying proportions. For instance, ground ivy has no tannoid, but it has a bitter principle, and the same is the case with thyme, balm, and various mints; but sage, skull cap, and hemp nettle contain tannoid and little or no amaroid. So also in the order Compositæ various species of Artemisia abound in bitter principles, but have no tannoid or even tannin; where the latter does occur, as in numerous Cynarocephalæ, its quantity is nearly always scanty. Hence it might be suggested that the decomposition of the tannoids would give rise to the bitter principles, and it seems quite possible that certain of the saponins and the alkaloids may originate in some such way. Thus the entire order Umbelliferæ seems to produce caffetannin in considerable quantities without much association of tannoid therewith, the latter in this case being converted into some sort of a poisonous rather than a harmless bitter principle. However, these suggestions are thrown out here mainly as grounds for further research, the actual analyses so far conducted yielding promise of important and interesting conclusions.

The Fat-oil in Plants.

As regards certain aspects this subject has been only superficially studied or considered, although it is of the highest interest and importance. According to Röhmann the fat of animals is not a degenerate product of cell protoplasm, and Gautier states that fat proceeds from the incomplete deassimilation (*i.e.*, by hydration, and not by oxidation) of the animal albumenoids. In plants, however, it is decidedly a product of assimilation which is wanting in no organ. But here the question arises, Is it ever a product of protoplasmic degeneracy? Some authorities seem to think it is so, sometimes at least. For instance, the refractive oily globules which are interposed in the cells where chlorophyll abounds in the winter leaves of ivy, yew, spruce fir, &c., are products of the degradation of the cell plasma due to the lowering of the temperature (Emile Mer); the fat oil which fills he entire cavity of the oleiferous hyphæ in the Amanita genus of fungi seems derived from a fatty degeneration of the protoplasm (Fayod); in autumn the chlorophyll undergoes a kind of oily transformation very comparable to the fatty degeneration which sometimes occurs in animal tissues (Mesnard). On the other hand, as respects the formation of the oil in olives, Spampani declares that it is not a degeneration product of the protoplasm, and this would seem to be the prevalent opinion as to the formation of fat-oils in seeds, fruits, and embryonal organs generally. Then, again, there are questions as to whether the fats are derived from the organised living protoplasm or from the dead unorganised proteid? Is the formation of fat direct and straight away; or do fatty acids first make their appearance, and then subsequently combine with glycerol to form fats? It seems to me that the latter is not the case, else more fatty acids would be extracted from the plant by benzene, &c., than what in my experience ever occurs. True, many analysts have concluded that plant fat is rich in unsaturated fat acid, and is thereby distinguished from animal fat; but it is probable that, in some cases at least, these so-called fat acids may have been originally hydrocarbons which oxidise rapidly in the air when removed from the tissues. It would appear, however, that the chief scientific interest of the vegetable oil centres about the origin of chlorophyll. I have already in these notes expressed a hint that chlorophyll cannot be formed in the leaf without the concurrence and assistance of fat-oil. According to Schrotter-Kristelli, "it is probable that by continued reducing action cholesterol yields yellow, and finally green, colouring matters (chlorophyll)." The latter has been recognised as a derivative of pyrolline by Schunck and others, and hence that the basis of blood pigment and of leaf pigment is the same; but it is absolutely certain that the cause and mode of formation of these two substances are entirely different; in fact, it would seem that chlorophyll originates in a way absolutely unique. It is produced within a globule of dense protoplasm which invariably encloses oil as a main ingredient, and which gives off oxygen only in the light. At the same time the globule is alive, *i.e.*, it contains a certain amount of water, and, moreover, as Gautier affirms, the phenomena of dehydration may be produced in the organised and living protoplasm within the cell and never outside of it, and indeed are produced more powerfully in plants than in animals. It is quite conceivable that under all these circumstances a powerful process of dehydration, rendered far more full and complete by the saving presence of oil, would induce the formation of a highly reductive product such as chlorophyll eminently is.

On Oxydases.

The craze of the moment among a certain class of biochemists is what is termed oxydase, a kind of ferment discovered by Bertrand in 1895, although in 1893 Lindet had suspected the existence of something of the kind contained in the crab apple. It is only necessary here to consider some of the evidence on which the existence of a special oxidising agent suppose to operate outside the living organism is based. Lindet states that boiled apple juice remains uncoloured in the air, and that a cooked apple when cut or bruised also does not redden. On the other hand, the fresh white slices may be washed with boiling water till all soluble tannin is removed, and yet as soon as they are exposed to the air they become red. In other words, the boiled extracted juice containing both oxydase and tannin does not colour, because perhaps the ferment is precipitated; but when the slices are practically exposed to the same treatment it does not relinquish its oxidising power, and hence the tissue reddens as if nothing had happened. How in the latter case the oxydase acts is not explained, for undoubtedly the boiling hot water would coagulate and destroy it just as it does in the former case. The truth of the matter, however, seems to be that the juice either within or outside of the apple is, by cooking

or boiling, rendered inert to aerial oxidation, the tannin under these conditions being rendered non-reductive by the action of the acids, &c., present in the liquid; and when the slices are washed with boiling water the whole of the tannic ingredients are by no means removed. In fact, fibro-vascular bundles are profusely scattered throughout the entire tissue of the mesocarp of the apple, and the tannin of the Rosaceæ has a special affinity for vegetable fibre, so much so, indeed, that when once adherent thereto, it cannot be removed by boiling alcohol or water or by dilute caustic soda, as is clearly shown in the analysis of the marsh cinquefoil, &c. There is no organisation in the pressed out juice of fruits, and the supposed action of oxydases on tannins, phenols, &c., therein is not a respiratory phenomenon. In short, the opinion expressed by Gautier in 1897 still holds the field, viz., that "oxidising diastases, being intimately united to the living protoplasm, have not hitherto been distinctly separated therefrom." And the dictum of Pasteur that "oxygen imparts to the cells an activity whence they derive the power of action beyond the influence of free oxygen, in the manner of the ferment-cells," cannot be ignored and is not sufficiently realised. Indeed, the special conditions of the medium are preponderant in these special cases of oxidising energy, and an aldehyde may act in a way hardly distinguishable from that of an oxydase, provided only that the conditions are favourable. But at bottom it is very questionable if the respiratory phenomena of the living organism depend on anything at all but its own inherent vital energy.

The Bearberry (Arbutus uva-ursi).

The glamour of romance, I having seen this plant carpetting the rocky bed of a wild sequestered valley in the Scottish Highlands, superadded to a touch of scientific curiosity, induced me to analyse the leaves thereof. Several analyses of these organs have already been published, one of which reports the presence of much gallic acid; Meisner states that there is 1·2 per cent gallic acid and 36·4 tannin, which latter figure is brought down to 14 by another analyst; in 1898 Perkin isolated therefrom gallotannin, and also gallic and ellagic acids; he thinks also that their colouring matter is quercetin and probably myricetin. Do these analyses exhibit aromatic substances already preformed, or do some of these latter become evolved by a specially violent method of treatment? Having extracted the powdered leaves with boiling benzene, they were then boiled twice with strong methyl alcohol, and the aqueous solution of these latter extracts was tested for tannins, &c., as usual. The result was quite conclusive as regards gallotannin; there was also a clear indication of a tannoid in no respect different from quercitrin; but the reactions of gallic or ellagic acids were not forthcoming. On fusing a portion of the extract with potass there were found pyrogallol and a quantity of phloroglucol much too large for the quantity of gallotannin acted upon, and hence the presence of a tannoid was so far confirmed. Another remarkable feature of these leaves was that, although they had been gathered some nine months previous to analysis, they still retained a notable amount of starch, but no oxalate of calcium was obtained, and the arbutin had all disappeared. The analysis proved very interesting in other respects. It is known that in the Central Alps a near relative, viz., *A. alpina*, assumes in autumn a vivid scarlet coloration, one of the most beautiful reds of any autumnal foliage of the world; but it is difficult to understand how this pigment proceeds from gallotannin as a chromogen. In fact, I have myself seen an extremely fiery red autumn tint on a species of azalea which contained only an iron-greening, phlobaphenic, catechol-phloroglucin tannin, according to my own analysis. Again, a member of that band of botanists who classify plants on the basis of evolution and anatomy, but reject chemistry, has recently suggested that the bilberry, bearberry, &c., should be removed from the order Ericaceæ (heaths) altogether. Now, there is no gallotannin in the bilberry, or in the heather. In an analysis published by Kanger in 1902 of the cowberry he reports the presence of gallic and ellagic acids, not as such, but as arising by the decomposition of the tannin, which he says on potass-fusion or dry distillation yields quinol, but this phenol almost certainly arises from arbutin (not always present), and not from tannin. I found that in the products of potass-fusion of the tannins of the azaleas and of bilberry respectively, the phloroglucol was in excess in the former case, *i.e.*, in the case where the autumnal red is excessively vivid, whereas with the bilberry the protocatechuic acid was predominant.

Patterdale, Westmorland.

PREPARATION OF THE NITRITES OF THE PRIMARY, SECONDARY, AND TERTIARY AMINES BY THE INTERACTION OF THE HYDROCHLORIDES OF THE BASES AND ALKALI NITRITES.

Explanation of the Action of Nitrous Acid on the Amines.

(Part I.).

By PANCHANAN NEOGI, M.A., Senior Professor of Chemistry, Government College, Rajshahi, Bengal, India.

(Concluded from p. 55.)

Steam Distillation in Vacuum.

The temperature of the bath was maintained at 80° to 85°. One grm. of the hydrochloride gave as the first distillate measuring 202 cc., which contained 0·38 grm. of benzylammonium nitrite. The solution was neutral to litmus and contained no nitrate. There was a faint smell of benzyl alcohol. 100 cc. of the first distillate when crystallised in four vacuum desiccators gave white deliquescent crystals of benzylammonium nitrite, soluble in water and alcohol.

0·1376 gave 24·4 cc. N_2 at 29° and 754 mm. (made up to 10 cc., of which $2\frac{1}{2}$ cc. = 6·1 cc. N_2); hence N ("nitritic") = 9·5 per cent. $C_6H_5.CH_2.NH_2.HNO_2$ requires N ("nitritic") = 9·0 per cent.

The solid nitrite was also obtained after concentrating the distillate on the water-bath to a small bulk. 200 cc. of the distillate was evaporated to 5·2 cc. only, when 62·8 per cent of the benzylammonium nitrite still remained in the solution. 310 cc. of the distillate was evaporated to 26·2 cc., when 84·5 per cent of the nitrite remained as such. The crystals of benzylammonium nitrite thus obtained were contaminated with small quantities of benzyl alcohol.

Interaction between Piperidinium Hydrochloride and Sodium or Potassium Nitrite. Sublimation in Vacuum

One or 2 grms. of the hydrochloride purified from absolute alcohol (Cl = 29·8 per cent found, Cl = 29·2 per cent calc.) were taken and mixed as usual with sodium or potassium nitrite. The temperature of the bath was maintained at 50° during the evaporation to dryness. No gas collected in the nitrometer. When the liquid was completely evaporated to dryness the neck of the flask was raised, and the temperature was also raised to 75° to 80°. A very small quantity of white crystals was observed to sublime in the cooler parts of the neck of the flask. The temperature was not allowed to rise above 90°. No gas collected in the nitrometer. The liquid in the test-tube also contained nitrite. The sublimate was washed out and tested, then mixed with the distillate in the test-tube and crystallised in the vacuum desiccator, when colourless deliquescent crystals of piperidium nitrite were obtained free from chloride.

Next, the water-bath was substituted by a sulphuric acid bath, and the temperature raised to 100° and above. The salt in the neck of the flask melted, and gradually

was turned into a reddish yellow liquid which readily gave Liebermann's nitroso-reaction. This liquid was therefore nitroso-piperidine, and, as pointed out before (Neogi, *Trans. Chem. Soc.*, 1911, xcix., 1600), is obtained by the decomposition of piperidinium nitrite according to the following equation :—$C_5H_{11}N.HNO_2 = C_5H_{10}N.NO + H_2O$. No gas collected in the nitrometer.

Steam Distillation in Vacuum.

Using 1 grm. of the hydrochloride the first distillate, 210 cc., contained 0·46 grm. of the nitrite, distillation being effected at 70°, almost quantitative yield being obtained in 520 cc. of the distillate. The solution can be evaporated to a small bulk without appreciable decomposition. 230 cc. of the distillate were evaporated to 26·5 cc., which contained 92·6 per cent of the nitrite undecomposed. The solution when crystallised in a vacuum desiccator gave deliquescent crystals of piperidinium nitrite, readily soluble in water and alcohol, and almost insoluble in ether (Neogi, *Trans. Chem. Soc.*, 1911, xcix., 1600).

0·0874 gave 18·0 cc. N_2 at 27° and 760 mm. (made up to 10 cc., of which 2 cc. = 3·6 cc. N_2); hence N_2 ("nitritic") = 11·2 per cent. $C_5H_{11}N.HNO_2$ requires N_2 ("nitritic") = 10·6 per cent).

In this way from 1 grm. of the hydrochloride from 0·4 to 0·6 grm. of the nitrite can easily be prepared.

Methylammonium Hydrochloride and Sodium or Potassium Nitrite.

The nitrites of the primary, secondary, and tertiary alkylamines are less stable than the nitrites described before. Of these nitrites, however, diethylammonium nitrite and triethylammonium nitrite sublime when heated in a vacuum with or without decomposition. Other nitrites of this series decompose more or less readily in the solid or liquid condition when heated in a vacuum. The following experiments show that, though these nitrites in the solid or liquid condition are more or less unstable, they are fairly stable *in solution*, and, in fact, this solution may be concentrated on the water-bath without great loss.

Steam Distillation in Vacuum.

The hydrochloride was as usual exhausted with small quantities of absolute alcohol and analysed (Cl = 52·1 per cent found, Cl = 52·6 per cent calc.).

There was scarcely any action on mixing. The temperature of the bath was maintained between 55° and 60°. Using 1 grm. of the hydrochloride the first distillate amounting to 215 cc. contained 0·52 grm. of methylammonium nitrite. There was no chloride or smell of alcohol in the distillate, which was neutral to litmus. The mercury level in the manometer remained almost constant, showing that very little decomposition took place. The solid nitrite was obtained as deliquescent, colourless crystals slightly tinged greenish, by evaporating 100 cc. of the first distillate to dryness in four vacuum desiccators. The solid nitrite was also obtained after concentrating the distillate on the water-bath. 180 cc. of the distillate containing 0·44 grm. of the nitrite when concentrated to only 11·2 cc. still contained 81·2 per cent of nitrite. When this concentrated solution was crystallised in a vacuum desiccator the solid nitrite was obtained in a fairly pure condition, only contaminated with very small quantities of the nitrates. As the decomposition product of methylammonium nitrite is methyl alcohol which is dissolved in the sulphuric acid of the desiccator, this rapid method of obtaining the nitrite is recommended as a method of preparation.

0·1392 gave 44·0 cc. N_2 at 30° C. and 755 mm. (made up to 10 cc., of which 1 cc. = 4·4 cc. N_2); hence N_2 ("nitritic") = 17·1 per cent. $CH_3.NH_2.HNO_2$ requires N_2 ("nitritic") = 18·0 per cent.

Ray and Rakshit (*Trans. Chem. Soc.*, 1911, xcix., 1018) have shown that methylammonium nitrite decomposes mainly into methyl alcohol and nitrogen. These are also the products of the interaction of nitrous acid and methylamine, so that methylammonium nitrite is evidently the intermediate compound in this interaction, which decomposes according to the equation—

$$CH_3.NH_2.NHO_2 = CH_3.OH + N_2 + H_2O.$$

Interaction between Ethylammonium Hydrochloride and Sodium or Potassium Nitrite.

The method of preparation and decomposition of the nitrite of this primary amine is identical with that of methylamine. There was no action when cold solutions of ethylamine hydrochloride (Cl = 42·8 per cent found, Cl = 43·5 per cent calc.) and sodium or potassium nitrite were mixed. The temperature at which distillation was conducted was 55° to 60°. The distillate contained no chloride or alcohol and was neutral in reaction. Two grms. hydrochloride yielded 0·69 grm. of the nitrite in the first distillate amounting to 160 cc. The liquid nitrite was obtained by evaporating 100 cc. of the first distillate in four vacuum desiccators without previous concentration as a colourless liquid slightly tinged yellow, readily soluble in water and alcohol.

0·1542 gave 43·0 cc. N_2 at 30° and 755 mm. (made up to 10 cc. with water, of which 1 cc. = 4·3 cc. N_2); hence N_2 ("nitritic") = 14·9 per cent. $C_2H_5.NH_2.HNO_2$ requires N_2 (nitritic") = 15·2 per cent.

The liquid nitrite was also obtained after concentrating the distillate on the water-bath. 224 cc. of the distillate was concentrated to 27·2 cc., when 84·6 per cent of the nitrite remained as such, the rest either evaporating with the steam or decomposing. As the principal decomposition product of ethylammonium nitrite is ethyl alcohol which is absorbed in the vacuum desiccator, the nitrite thus obtained was practically pure, containing small quantities of the nitrate.

The products of decomposition of ethylammonium nitrite (Ray and Rakshit, *Trans. Chem. Soc.*, 1911, cxix., 1472) are mainly ethyl alcohol, nitrogen, and water, which are also the end-products of the interaction of nitrous acid and ethylamine. Evidently the end-products are the decomposition products of ethylammonium nitrite, which decomposes according to the equation—

$$C_2H_5.NH_2.HNO_2 = C_2H_5.OH + N_2 + H_2O.$$

Interaction between Dimethyalmmonium Chloride and Sodium or Potassium Nitrites.

The preparation of the nitrites of two secondary alkylamines was then undertaken. Dimethylammonium nitrite is a liquid and comparatively unstable (Ray and Rakshit, *Trans. Chem. Soc.*, 1911, xcix., 1472), while diethylammonium nitrite is a solid, and sublimes unchanged when heated in a vacuum (*Trans. Chem. Soc.*, 1912, ci., 612).

Steam Distillation in Vacuum.

Two grms. of dimethylammonium chloride purified from alcohol (Cl = 43·9 per cent found, Cl = 43·7 per cent calc.), 1 grm. gave 0·56 grm. of the nitrite in the first distillate amounting to 120 cc., distillation being conducted at 55° to 60°. When 100 cc. of the distillate was kept in four vacuum desiccators as described above, dimethylammonium nitrite was obtained as a pale yellow liquid, very soluble in water and alcohol.

0·1848 gave 50·5 cc. N_2 at 30° and 753 mm. (made up with water to 10 cc., of which 2 cc. = 10·1 cc. N_2); hence N_2 ("nitritic") = 14·7 per cent. $(CH_3)_2.NH.HNO_2$ requires N_2 = 15·2 per cent.

150 cc. of the distillate containing 0·303 grm. of the nitrite was evaporated to 10·2 cc., when 64·2 per cent of the nitrite was found to be present. The liquid nitrite thus obtained was contaminated with small quantities of the nitroso-compound.

The principal decomposition product being nitrosodimethylamine (*Trans. Chem. Soc.*, 1912, ci., 612), it is evident that dimethylammonium nitrite is an intermediate compound in the interaction between nitrous acid and dimethylamine.

Interaction between Diethylammonium Chloride and Sodium or Potassium Nitrite. Sublimation in Vacuum.

It has already been mentioned that diethylammonium nitrite is a stable salt, and sublimes unchanged when heated in a vacuum. Ray and Rakshit have not determined the temperature at which sublimation of the pure nitrite takes place nor the temperature at which decomposition of the salt commences. When heated in a vacuum the nitrite commences to sublime in colourless crystals at 55°, and at 55° to 65° a good quantity collects in the cooler parts of the tube. When the temperature is further raised the salt melts at 74° to 76° into a pale yellow liquid which solidifies on cooling. If, however, the temperature is raised to 90° and above, a pale yellow oil is obtained which does not solidify on cooling and which is insoluble in water. This liquid gives nitroso-reaction, and is evidently nitroso-diethylamine.

Sublimation in the Töppler vacuum with 2 grms. of the hydrochloride (Cl = 32·8 per cent found, Cl = 32·4 per cent calc.) mixed with sodium or potassium nitrite does not give good results, only very small quantities subliming at 60° to 65°. The liquid in the test-tube, however, gave tests of the nitrite.

Steam Distillation in Vacuum.

Almost quantitative results are, however, obtained by submitting a solution of the mixture to vacuum distillation in steam.

0·5 grm. of the hydrochloride gave 0·38 grm. of the nitrite in 216 cc. of the distillate. Using 2 grms. of the hydrochloride 280 cc. of the distillate gave 0·72 grm. of the nitrite, which was evaporated to 7 cc. only on the water-bath, when 88·3 per cent of the nitrite remained as such. The temperature at which distillation was carried on was 65° to 70°. The preparation of the solid nitrite in a pure condition can be very easily done after concentrating the distillate on the water-bath to about 25 cc. The crystals were white, deliquescent, very soluble in water and alcohol. No nitroso-compound accompanied the crystals.

0·1062 gave 23·0 cc. N_2 at 30° and 755 mm. (made up to 10 cc., of which 2 cc. = 4·6 cc. N_2); hence N_2 ("nitritic") = 11·62 per cent. $(C_2H_5)_2.NH.HNO_2$ requires N_2 ("nitritic") = 11·66 per cent.

The main decomposition product of diethylammonium nitrite being nitroso-diethylamine, which is also the end-product of the interaction of diethylamine hydrochloride and alkali nitrite, it is evident that diethylammonium nitrite is the intermediate compound hitherto not isolated from the mixture.

Interaction between Trimethylammonium Chloride and Sodium or Potassium Nitrite.

Of the nitrites of the two tertiary amines examined, triethylammonium nitrite is a stable compound which sublimes on heating in a vacuum though with decomposition. Trimethylammonium nitrite does not sublime in a similar manner.

Steam Distillation in Vacuum.

The distillation was conducted at 55° to 60°, 2 grms. of the hydrochloride (Cl = 37·8 per cent found, Cl = 37·2 per cent calc.) being used. 160 cc. gave 1·1 grm. of the nitrite, almost quantitative yield being obtained in 450 cc. The pure nitrite was obtained on crystallisation of 100 cc. of the distillate in four vacuum desiccators at the temperature of the laboratory.

0·1300 gave 29·7 cc. N_2 (made up to 22 cc., of which 2 cc. = 2·7 cc. N_2) at 30° and 755 mm.; hence N_2 ("nitritic") = 12·21 per cent. $(CH_3)_3N.HNO_2$ requires N_2 ("nitritic") = 13·20 per cent.

On evaporating 210 cc. of the distillate containing 1·0 grm of the nitrite to 18 cc., 61·1 per cent of the nitrite remained as such. Appreciable quantities of the nitrate accompanied the nitrite.

It is incorrect to suppose, as is generally done, that there is no reaction between nitrous acid and a tertiary amine. What such statement really means is that no specific reaction takes place other than what usually takes place between nitrous acid and a base, the corresponding nitrate and nitric oxide being formed by the decomposition of the unstable nitrous acid according to the equation $3HNO_2 = HNO_3 + H_2O + 2NO$, the nitric acid combining with a part of the free amine.

In order to corroborate this statement, 1 grm. of the hydrochloride mixed with molecular quantities of sodium nitrite was dissolved in a small quantity of water and evaporated to dryness, using the apparatus described before for sublimation *in vacuo*. The solution was evaporated to dryness at 50°; very little gas collected in the nitrometer. The temperature was then raised to 60° and then to 70°. A gas collected in the nitrometer which consisted mainly of nitric oxide mixed with small quantities of nitrogen and the vapours of the free amine. The distillate in the test-tube was strongly alkaline in reaction and smelt of trimethylamine, and also contained a mixture of the nitrite and nitrate.

The formation of the decomposition products can very readily be explained in the following manner:—During the interaction trimethylammonium nitrite is formed, which distils in vacuum with the steam in small quantities as such. Part of the trimethylammonium nitrite, however, dissociates into the free amine and nitrous acid,—

$$(CH_3)_3N.HNO_2 = (CH_3)_3N + HNO_2.$$

The nitrous acid again decomposes into nitric acid and nitric oxide, according to the equation given above, the nitric acid combining with a portion of the free amine forming the nitrate, while part of the free amine remains uncombined.

The decomposition of pure trimethylammonium nitrite has been studied by Ray and Rakshit (*Trans. Chem. Soc.*, 1911, xcix., 1474), who have found that the same decomposition products, viz., the nitrate, the free amine, and nitric oxide, are obtained.

Interaction between Triethylammonium Chloride and Sodium or Potassium Nitrite. Sublimation in Vacuum.

One or 2 grms. of the hydrochloride purified from alcohol (Cl = 26·7 per cent found, Cl = 25·9 per cent calc.) were used with sodium or potassium nitrite. The solution was evaporated to dryness at 50° without decomposition. The temperature was then gradually raised to 70° and then finally to 90°. The evolution of gas was very brisk. The gas was found to consist mainly of nitric oxide with small quantities of nitrogen. No appreciable sublimation was observed, as water being one of the products of decomposition the small quantity that usually sublimed was dissolved in the water. The distillate in the test-tube was strongly alkaline and strongly smelt of the free amine. Besides the amine, the distillate contained nitrite mixed with the nitrate. Here, as in the case of trimethylamine, the principal products of the interaction of nitrous acid and the tertiary amine are free amine, nitrate, and nitric oxide. The explanation is also the same, viz., that triethylammonium nitrite is formed, part of which distils unchanged with the steam and part dissociates into triethylamine and nitrous acid, the latter decomposing into nitric oxide and nitric acid, which forms the nitrate.

The decomposition of pure triethylammonium nitrite has been studied by Ray and Rakshit (*Trans. Chem. Soc.*, 1912, ci., 218), who have found that the same decomposition products are obtained along with small quantities of nitrous oxide and alcohol.

Vacuum Distillation in Steam.

The temperature at which distillation was conducted was 65° to 70°. One grm. hydrochloride gave, in 180 cc. distillate, 0·48 grm. of the nitrite. 230 cc. of the distillate was evaporated to 28·5 cc. on a water-bath, when 92·2 per cent of the nitrite remained undecomposed. The crystals obtained from the concentrated liquid were white,

deliquescent, very soluble in water and alcohol. The nitrite was also obtained in a pure condition on concentrating 100 cc. of the distillate in four vacuum desiccators at ordinary temperature.

0·1116 gave 19·2 cc. N_2 at 30° and 754 mm. (made up to 10 cc. with water, of which $2\frac{1}{2}$ cc. = 4·8 cc. N_2); hence N_2 ("nitritic") = 9·2 per cent. $(C_2H_5)_3.N.HNO_2$ requires N_2 ("nitritic") = 9·4 per cent.

Both trimethyl- and triethyl-ammonium nitrites are slowly changed into the nitrate on keeping as a result of their dissociation.

Interaction between Tetramethylammonium Nitrite and Sodium or Potassium Nitrite. Vacuum Distillation in Steam.

While attempting to prepare the nitrites of tetralkylammonium bases, it was found that tetramethylammonium nitrite does not volatilise with steam in vacuum, though the distillation was carried on at varying temperature from 60° to 100°. Work on other amines is in progress.

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MELTING-POINTS OF THE REFRACTORY ELEMENTS.*

I. ELEMENTS OF ATOMIC WEIGHT FROM 48 TO 59.

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THE elements included in this list are the iron group: nickel, cobalt, iron, manganese, and chromium, and also vanadium and titanium. In subsequent papers results will be given on other refractory elements now being studied, and it is hoped eventually to include all the available refractory elements in this series of melting-point determinations. The method mainly used is that of the micropyrometer, which, with substances that melt sharply, as nickel, cobalt, and iron, permits working to a precision of 1 or 2° with a few thousandths of a milligrm. of the material. ("A Micropyrometer," by G. K. Burgess, *Journ. Washington Academy of Sciences*, 1913, iii., 7; *Phys. Zeit.*, 1913, xiv., 158; *Bull.* Bureau of Standards, 1913, ix., 475.)

An estimation of the melting-points of the iron group elements was made some years ago by a similar but less sensitive method at a time when none of these melting-points was well known. ("Melting-points of the Iron Group Elements by a New Radiation Method," by G. K. Burgess; *Bull.* Bureau of Standards, 1907, iii., 345.) The object of these earlier measurements was primarily to demonstrate the convenience and reliability of the method, especially for those elements which can be obtained pure only in minute quantities. It is believed that the present series of determinations, with the improved apparatus, will contribute to a more exact knowledge of these melting-points. The melts were made for the most part in pure hydrogen, and except for titanium, were taken on platinum strips 6 to 8 cm. long, 4 mm. wide, and 0·01 or 0·02 mm. thick. Manganese was also melted on nickel strips and titanium was melted on iridium strips.

Calibration with Nickel and Palladium.—For melts on platinum the pyrometer was calibrated in terms of the melting-points of nickel and palladium. The melting of these metals is extremely sharp on platinum and they appear to show no alloying until they melt. It is assumed that they melt on platinum at the same temperatures as in crucibles; this we have found to be the case for nickel, palladium, platinum, and iron. Numerous observations were made with various metals upon the possible effects on the melting-point determinations of alloying with the platinum strip. We are convinced, that except possibly in some cases which we shall not consider here in which there may be a chemical reaction among the materials in the furnace, as for example when silicon, platinum, and hydrogen are together, there is no significant alloying effect with the apparatus and materials as we use them.

The melting-points of both nickel and palladium may be considered as well established by several series of measurements. (See Day and Sosman, Carnegie Institution of Washington, Pub. 157, 1911; Waidner and Burgess, *Bull.* Bureau of Standards, 1907, iii., 163.) We have made an independent optical determination of the nickel melting-point in hydrogen with an Arsem furnace. (*Journ. Am. Chem. Soc.*, 1906, xxviii., 921.) The nickel was melted in a magnesia crucible contained within an out-glazed, closed-end porcelain or kaolin tube. Temperatures were measured with a Holborn-Kurlbaum form of Morse pyrometer which had been calibrated by Dr. Kanolt at the melting-points of antimony (630°), Ag_3Cu_2 (779°), silver (960·5°), copper (1083°), and diopside (1391°). Five observations by Dr. Kanolt on the melting-point of platinum with this pyrometer gave 1755° ± 5 in an iridium furnace, or in exact agreement with the generally accepted value. (See Day and Sosman, *loc. cit.*)

For nickel, four observations gave us 1449°, 1450°, 1449°, 1449° in the Arsem furnace, by the method of optical heating and cooling curves, values which are close to Day and Sosman's value, 1452°. (C. W. Kanolt, Tech. Paper No. 10, Bureau of Standards, 1912.) Four observations of the melting point of nickel on iridium with the micropymeter gave us 1452°.

With the long filament pyrometer lamps used, the equation $\log c = a + b \log T$ (in which c = current and T = absolute temperature and b is very nearly unity) is sufficient for very considerable temperature ranges, and permits a calibration in terms of two temperatures only, *i.e.*, nickel and palladium. (Pirani, *Verh. Phys. Ges.*, 1910, xii., 323.) Applying this equation by extrapolation to the determination of the platinum melting-point by observing the melting of platinum strips mounted as usual for taking metal melts, we obtained 1755° ± 5 from six observations. The values found for diopside (1391°) and anorthite (1549°) by Day and Sosman were also exactly reproduced by us with the micropyrometer.

The metals actually used for calibration in hydrogen were "Kahlbaum" electrolytic nickel (MP = 1452°) and pure Heraeus palladium (MP = 1549°), both of the same grade as used by Day and Sosman. (Day, Sosman, and Allen, *loc. cit.*; the analysis by Dr. Allen of these products gave the nickel as 99 835 pure and the palladium 99·975). A sample of their palladium gave exactly the same melting-point as ours. In controlling the constancy of the pyrometer lamps and studying the reproducibility of the melts some 35 observations were taken of nickel and 20 of palladium. The various metals were not studied in regular order but were mixed as indiscriminately as possible, with observations on the standard points, nickel and palladium.

Iron.—Pure electrolytic iron from three sources and as many different methods of preparation were used, namely, from Prof. C. F. Burgess (99·97 per cent Fe), from Langheim-Pfanhauser Werke A. G. (99·98 per cent Fe), and from a sample (99·99 per cent Fe) prepared by Mr. J. R. Cain of this Bureau. "Kahlbaum" iron in powdered form and iron reduced on the platinum strip in hydrogen from Kahlbaum iron oxide were also used.

TABLE I.—*Melting-point of Iron in Hydrogen by Micropyrometer.*

Electrolytic, C. F. Burgess	1538°, 1537°, 1530°, 1534°, 1530°, 1532°
Mean	1533°
Electrolytic, Langheim-Pfanhauser	1524°, 1532°, 1534°, 1534°, 1535°
Mean	1532°
Electrolytic, Cain	1533°
Powder, "Kahlbaum"	1534°
From Oxide, "Kahlbaum"	1532°

* To appear in the Bulletin of the Bureau of Standards. From *Journal of the Washington Academy of Sciences*, iii., No. 13.

The mean value is 1533° ± 1°. This is somewhat higher than all other recent determinations, which range from 1502° to 1532°. In the Arsem furnace we obtained *in vacuo* 1531°, 1529°, 1531°, 1527°, and in hydrogen 1523° and 1527°.

Cobalt.—The cobalt used was cobalt "Kahlbaum" in the form of powder, Kahlbaum's Würfeln, cobalt reduced in hydrogen on the platinum strip from "Kahlbaum" cobalt oxide, and a sample kindly furnished by Messrs. Day and Sosman, cut from material which had been used for their determinations and which was originally powdered cobalt "Kahlbaum," shown by Dr. E. T. Allen to be 99·951 per cent cobalt. (Day, Sosman, and Allen, *loc. cit.*) The mean is 1477° ± 2.

Table II.—*Melting-point of Cobalt by Micropyrometer.*

"Kahlbaum," powder and Würfeln together	1478°, 1479°, 1482°, 1476°, 1475°, 1476°, 1478°
Mean	1478°
Co from the oxide "Kahlbaum"	1475°, 1478°
Day and Sosman's sample	1474°, 1478°, 1478°

Three observations taken in the Arsem furnace each gave for the melting-point of cobalt 1478°. Finally two melts of cobalt on iridium gave with the micropyrometer 1477° and 1478°. The value of the cobalt point which Day and Sosman found is 1490° in a nitrogen atmosphere.

Chromium.—Strictly pure chromium was not available, and it is difficult to locate exactly the melting-points of an impure viscous substance. Observations were taken on two samples from Kahlbaum and on one from Dr. H. Goldschmidt, all of a purity probably not greater than 98 per cent.

Table III.—*Melting-point of* (98 *per cent ?*) *Chromium by Micropyrometer.*

Kahlbaum I.	1527°
Kahlbaum II.	1536°, 1513°, 1513°
Goldschmidt	1514°, 1524°

As the best representative value we may take 1520°. The melting-point of pure chromium, however, may well be above that of iron, as may be shown by a consideration of the well-known formula for lowering the freezing-point by metallic impurities. On the other hand, the value 1520° may be more nearly correct if the oxides present do not lower but raise the chromium melting-point, as was found in the case of vanadium by Ruff and Martin. (Ruff and Martin, "Uber reines Vanadin," *Zeit. Angew. Chem.*, 1912, xxv., 49.) If chromium is melted, for example, in a slightly oxidising atmosphere or in impure hydrogen, an apparent melting-point above that of platinum may be obtained.

Manganese.—We have not been able to obtain pure manganese, and the impure samples from Kahlbaum and from Goldschmidt are even more sluggish than chromium. The Goldschmidt manganese was from a sample of about 97·5 per cent pure. Melts were taken both on platinum and on nickel strips with the micropyrometer, using gold (1063°) and palladium as calibration points. Those on nickel were less satisfactory, due apparently to evaporation of nickel.

Table IV.—*Melting point of* (97·51) *Manganese by Micropyrometer.*

Kahlbaum	on Pt, 1242°; on Ni, 1221°
Goldschmidt	on Pt, 1261°, 1264°, 1279°; on Ni, 1254°

The mean is 1254°, which is probably lower than the melting-point of strictly pure manganese by 20°.

Vanadium.—Dr. v. Wartenberg, of Berlin, kindly sent us some 97 per cent vanadium prepared by him from the suboxide by the alumino-thermic method with calcium; it contains traces of Ca, Al, and Fe. Professor Wedekind, of Strassburg, also furnished us with a sample of his 97 to 98 per cent vanadium. We have also examined two samples purchased from Kahlbaum at different dates. None of the samples melts sharply, the substance being viscous; all samples show evidences of incipient melting many degrees below the temperature at which the melting is complete.

With the Kahlbaum samples, evidences of melting were apparent as low as 1500°; melting was complete at about 1720°, the samples showing evidences of non-homogeneity of composition.

With Dr. v. Wartenberg's and Professor Wedekind's vanadium the following results were obtained:—

Table V.—*Melting-point of 97 per cent Vanadium by Micropyrometer.*

97 to 98 per cent V from Wedekind, 1700°, 1757°, 1773°, 1717°

97 per cent V from v. Wartenberg, 1680°, 1691°, 1691° (pieces of about 0·001 mg.), 1685°, 1699°, 1705° (medium-sized pieces), 1725° (largest pieces).

Evidences of incipient melting were apparent at about 1650° with these materials. Other determinations of the vanadium melting-point range from 1680° to 1750°. We would place the vanadium melting-point at about 1720°, both from a consideration of our own and of other determinations.

Titanium.—Prof. M. M. A. Hunter, of Rensselaer Polytechnic Institute, kindly placed at our disposal a sample of pure titanium, which he had prepared from material furnished by the Titanium Alloy Manufacturing Company, of Niagara Falls. This titanium, analysed by Professor Hunter, contains only a trace of iron and no other detectable impurity. Professor Wedekind likewise kindly sent us two samples prepared by him of 94 to 95 per cent purity and one by Dr. v. Wartenberg. The colloid titanium of Wedekind melted at 1508° to 1451°, and his powdered titanium at 1452°. We also took observations on two samples from Kahlbaum, which were evidently quite impure, showing evidences of an extended melting range. For the Kahlbaum samples, the following melting-points were obtained:—1664°, 1724°, 1677°, 1737°, 1641°. The titanium of Hunter and of v. Wartenberg showed no signs of melting on platinum; their melting-points were taken on iridium strips.

Table VI.—*Melting-point of Titanium by Micropyrometer.*

Ti from Professor Hunter	1790°, 1785°, 1785°
Mean	1788°
Ti from Dr. v. Wartenberg	1778°, 1807°, 1815°
Mean	1800°

These melting-points are fairly sharp, and the location of the temperature was made by calibrating the micropyrometer for the iridium strip by taking observations on it of the melting of palladium (1549°) and of platinum (1755°).

Summary.—We have shown that the micropyrometer may be made an instrument of precision for the determination of the melting-points of refractory metals and salts; that in the case of the metals examined, the effect of alloying of microscopic particles on platinum and iridium is inconsequential until after melting which we have shown for nickel, cobalt, and iron to occur at the same temperature for minute particles on the strips as for considerable quantities in crucibles of magnesia.

Assuming the melting-points of nickel to be 1452°, palladium 1549°, and platinum 1755°, and the calibration curves of the pyrometer lamps of the form $\log c = a + b \log T$, for the range here studied, we have determined the melting-points of Fe, Co, Cr, Mn, V, and Ti with the micropyrometer and of Ni, Co, and Fe in quantity in the electric furnace, all melts having been taken in pure hydrogen and Fe also *in vacuo*. For Cr, Mn, and V, strictly pure materials were not available, and we can but estimate the melting-points of the pure elements.

Table VII.—*Melting points of Elements of Atomic Weight 48 to 59.*

Metal.	Melting-point with micropyrometer.	Purity (per cent).	Probable melting-point of pure element.
Nickel ..	1452° (a) 1449 (b)	99·835	1452° ± 3
Cobalt	1477 ± 2 1478 ± 1 (c)	99·951	1478° ± 5
Iron	1533 ± 1 (d) 1528 (b)	99·98 ± 0·01	1530° ± 5
Manganese ..	1255	97 to 98	1260° ± 20
Chromium ..	1520	98 to 99	1520° to >Fe
Vanadium ..	1720	97 to 98	1720 ± 20
Titanium ..	1794 ± 12	99·9+	1795 ± 15

(a) Assumed value on platinum strip; also observed value on iridium strip.
(b) Crucible melts in electric furnace.
(c) Crucible melts in electric furnace; also on iridium strip with micropyrometer.
(d) Five samples all agreeing to within 3°.

In the complete paper, the method is discussed more in detail and photomicrographs are given showing characteristics of the various melts.

THE INDEX TO CHEMICAL LITERATURE.

By L. H. Baekeland.

Under this title, the U.S. Patent Office has published a statement describing the work undertaken by the Classification Division, so as to enable rapid and complete searches to be made on any subject of chemical literature. This is a gigantic piece of work, embracing not merely patent literature, but practically all fields of chemical literature.

(Appendix K of the Report of the Investigation of the U.S. Patent Office, by the President's Commission on Economy and Efficiency, December, 1912. House of Representative, 62nd Congress, 3rd Session, Document No. 1110).

Before the chemical card index was commenced, anything like a complete search of the literature was practically impossible, and the validity of chemical patents was more or less in doubt; for, after the most elaborate search possible was made, a five-line paragraph in the files of some little known chemical journal published in Japanese, Russian, or other not readily understood language, would be sufficient if cited in court to invalidate the granted patent.

It will be several years before this card index is complete, although much assiduous work is being done on it. In the meantime, enough has already been accomplished that any one making a search on the literature of a chemical subject can save much labour and time by consulting the index of the Patent Office. It should be noted that the index is accessible not only to the examiners of the Patent Office, but to patent lawyers practising before the office, as well as to chemists and scientific workers all over the land. Hence, this card index is becoming a national monument to chemical literature.

For those not living too far away a visit to Washington to consult the index may prove the shortest and cheapest way to make a search in chemical literature. It would be highly desirable, however, if duplicates of this index could be obtained for the more important libraries all over the country. It is true that copying this card index would be rather expensive, but there is no doubt that the enormous value of such a copy would be fully worth the expense. Why could not some of the libraries of the country work together and have several copies printed at the same time, and thus distribute the cost of the task among themselves?

It is interesting to quote from the report mentioned above:—

"In planning the chemical card index, since it was manifestly impossible to index all chemical literature, it was decided to cover the work of the past by making a judicious selection of certain works of a general nature, such as the 20 volume work of Gmelin, the annual volumes of the Chemical Society of London, and the 4 volume edition of Watts's 'Dictionary of Chemistry,' Richter's 'Lexicon of Carbon Compounds,' and other works of that character; by indexing these works the literature of the past would probably be as completely covered as it could be by any plan which the office had the force and means available for accomplishing."

"For the future it was proposed to keep the abstract journals of the Chemical Society of London, the German abstract periodicals, *Berichte* and the *Centralblatt*, and other works of that character indexed up to date."

"Later, when the American Chemical Society, in 1907, commenced the publication of its very complete set of abstracts, it was determined to omit the periodicals in German and other foreign tongues, and retain in the card index only the yearly index volume of the Chemical Society of London in addition to the American abstracts."

The above reference to the usefulness of the abstracts of the American Chemical Society would be decidedly more satisfactory if it were not accompanied by the following statement:—

"The question has been raised whether the annual index of the Chemical Society of London is not duplicated by the work of the American abstractors to such an extent as to render it useless to include both publications in the index."

"It is found upon comparing the published list of the publications indexed by each set of abstracts as follows:—

Publications abstracted by the London Society ..	101
Publications abstracted by the American Society ..	516
Publications abstracted by the London Society not abstracted by the American	29

These 29 publications not covered by our American workers include the following, viz.:—German, 8; English, 12; Dutch, Swedish, and French, 2 each; and 1 each of Italian and Japanese.

"Comparing 6 pages of the English Society Index of 1909 with the corresponding American work of the same year it is found that out of 256 articles and monographs indexed by the English workers, 159 of these articles were not in any way referred to in the American Society Abstracts."

"These two facts together seem to fully answer the question, and show the necessity of including both works in the index."

May this criticism stimulate out American abstractors to greater zeal and accuracy, aside from the fact that many justified criticisms have been made that in some instances the abstracts are carelessly drawn up and give a very wrong idea of the originals.

Various difficulties were encountered in outlining a general plan for the index. If chemical bodies each had but one instead of several names, and if in chemical literature one never met with bodies as yet unnamed and therefore referred to by chemical formulæ only, then undoubtedly the dictionary plan pure and simple, with the names of the substances alphabetically arranged and the references to literature and patents collected under their proper titles, would answer every requirement, and would be, in fact, the only proper system to use. Practically, however, most bodies known to chemists have a plurality of names, and the names approved and used in prior decades are generally not the names in highest repute nor in ordinary use to-day, nor is it at all sure that the names now in use will in most or even in many cases remain in use in years to come.

Where a chemical compound has several names (as indeed is usually the case) were it possible to decide now

(which perhaps might be done) which one of them is, on good scientific grounds, the most appropriate for index purposes in view of present knowledge, and further (which of course could not be done), could one be assured that such name would remain the approved name for all future time, such title could, without hesitation, be now adopted as the indexing title, under which all references to literature or patents could be entered, and all other titles and names cross-referenced into it; but while this might be done now in certain cases, which and how many of these names now used and approved will remain in use in years to come is something that no one can at present determine. Evidently the dictionary plan, unmodified, was not the best, and some better system had to be devised not open to these objections.

The system adopted was based on the chemical formula. In establishing for the Patent Office a card index to chemical literature, it was therefore decided to use, as an indexing basis, the kind and number of the component atoms of a chemical compound, these being its most unvarying characteristics, being subject only to errors of chemical analysis, and being therefore the most stable and unchanging basis for any scheme for the indexing and digesting of chemical literature; a conclusion reached at about the same time independently by Richter, as illustrated in his since published "Lexicon der Kohlenstoff-Verbindungen," and by other later workers in this field, the Patent Office system differing from that of Richter in being simpler and of more general application.

It was found that the simplest, most certain, and most direct system, was to re-write the so-called empirical chemical formula in a particular manner; that is to say, to write the atoms in the alphabetical order of their chemical symbols, upon library catalogue cards of standard size, and place these cards, arranged in alphabetical order, in standard library cases. For example, take the following chemical compounds:—

$(CH_3)_2C_2H_2(NO_2)_2$	Dinitrobutane
$(CH_3)_2CHNO_2$ ..	Isopropylic nitrite
$KH_3C_2O_4$	Potassium acetate
CH_3Cl .	Methyl chloride
$Cu(AsO_2)_2$	Copper arsenite

Re-writing them and arranging them alphabetically by formulæ instead of titles, they are:—

As_2CuO_4	Copper arsenite
CH_3Cl ..	Methyl chloride
$C_2H_3KO_4$	Potassium acetate
$C_3H_7NO_2$	Isopropylic nitrite
$C_4H_8N_2O_4$	Dinitrobutane

It should be noted, however, that the compounds containing carbon and hydrogen, and broadly included in the domain of organic chemistry, constitute so large and important a class that it is fully justifiable to depart slightly from the strictly alphabetical arrangement of chemical symbols, and write C always first and H accompanying C always second, in order to bring more closely together in the index bodies more or less closely related in chemical and physical properties.

In practice, therefore, the following general rule has been followed in compiling the chemical card index of the Patent Office:—Reject water of crystallisation and re-write the empirical formula in the alphabetical order of the chemical symbols, except that in carbon compounds, C is to be written first and H second. Follow this re-written formula with the constitutional formula, when given, adding the water of crystallisation, if any, but arrange the cards alphabetically by the re-written formula.

The reason for disregarding water of crystallisation may be illustrated as follows:—The three bodies, Na_2SO_4 or anhydrous sodium sulphate, $Na_2SO_4+10H_2O$ or Glauber's salt, and the heptahydrated salt, $Na_2SO_4+7H_2O$, are in this way indexed under the same indexing formula, Na_2O_4S, and are thereby brought together, as they should be, for in solution they are chemically identical. If, on the other hand, water of crystallisation were taken into account for indexing purposes, the corresponding indexing formulæ would become Na_2O_4S, $H_{20}Na_2O_{14}S$, and $H_{14}Na_2O_{11}S$, respectively, and these three practically identical bodies would, in consequence, be widely separated in the index, which result would evidently be a very undesirable one.

The index was commenced and has been continued on the library-card catalogue plan, using the regular standard card, size 7½ by 12½ centimetres, or approximately 3 by 5 inches, without rulings except a single coloured horizontal line three-eighths of an inch below the top of the card—this for typewritten cards and cards upon which printed matter cut from books and periodicals is pasted. A limited use has also been made of cards having ruled lines, where for certain reasons the cards are written by hand.

I believe it would be very desirable to have an exchange of opinions on this subject in the correspondence column of this journal. It is our duty to assist by any helpful suggestions possible, the good work which is now being performed by the Washington Patent Office.—*Journal of Industrial and Engineering Chemistry*, v., No. 7.

THE ELECTRODEPOSITION OF TIN.*

By EDWARD F. KERN.

(Continued from p. 59).

III. *Electrodeposition of Tin by Separate Current* (continued).

10. Fearn recommends a bath which he prepared by dissolving 25 grms. of tartaric acid in about 400 cc. water, 75 gms. of caustic potash in about 400 cc. water, and 1·3 grm. of fused stannous chloride in 50 cc. of water. The caustic solution was added to the tin solution, then the tartaric acid solution mixed with it. Diluted to 1 litre, and electrolysed cold or hot. Thick bright deposit (McMillian-Cooper, "Electrometallurgy," 1910 Ed., p. 249).

11. Steele prepared an electro-tinning solution by dissolving 5·5 grms. of caustic potash, 16·5 grms. of potassium carbonate, and 66 grms. of sodium carbonate in 1 litre of water, after which he added 17·5 grms. of tin dioxide, 1 grm. potassium cyanide, and 1 grm. zinc acetate. Filtered before using (McMillian-Cooper, "Electrometallurgy," 1910 Ed., p. 249; Watt and Philip, "Electroplating and Electrorefining of Metals," 1911 Ed., p. 345).

12. An alkaline bath proposed by Elsner for tinning iron and steel articles is prepared by putting 11 grms. of tin bichloride in 1 litre of water, then adding a solution of potash lye of 10° B. until the precipitate is dissolved, and 10 grms. of potassium cyanide (Langbein-Brannt, "Electrodeposition of Metals," 1909 Ed., p. 440).

13. Good deposits of tin may be produced by dissolving 1·5 grm. of fused stannous chloride, 80 grms. of potassium carbonate, and 1 grm. of potassium cyanide, separately in water; then adding the cyanide solution to the tin solution, and finally stirring in the carbonate solution. Dilute to 1 litre. This solution is not a very good conductor of current, thus requiring a high voltage; still satisfactory deposits may be obtained (Barclay and Hainsworth, "Electroplating," 1912 Ed., p. 331).

14. Salzedes used a bath for tinning iron which he prepared by adding 10 grms. of potassium cyanide, 110 grms. of potassium carbonate, and 2·5 grms. of stannous chloride to 1 litre of water. By electrolysing with voltage at 4 to 5, a heavy dense deposit was rapidly obtained (Langbein-Brannt, "Electrodeposition of Metals," 1909 Ed., p. 441).

15. An electrolyte patented by Fearn in 1873 contained

* Paper presented at the Twenty-third General Meeting of the American Electrochemical Society, at Atlantic City, N.J., April, 1913. From the *Chemical Engineer*, xvii., No. 6.

1·2 grm. of fused tin bichloride, 111 grms. caustic potash, 111 grms. potassium cyanide, and 111 grms. of sodium pyrophosphate per litre. Each of these chemicals were separately dissolved in water; the tin solution was poured into the potash solution with constant stirring, then the cyanide solution was added, and finally the pyrophosphate solution. Electrolysed at ordinary temperature. Bright thick deposits were obtained. It was found necessary to add fused tin chloride to the bath from time to time, as the anodes were not dissolved as rapidly as the tin deposited (Watt and Philip, "Electroplating and Electrorefining of Metals," 1911 Ed., p. 345; McMillian-Cooper, "Electrometallurgy," 1910 Ed., p. 248).

16. The following solutions are capable of giving good white deposits upon all metals, and may be used cold:—

(*a*) Solution for electro-tinning brass, bronze, and copper; 7·5 grms. of caustic potash, 7·5 grms. of stannous chloride, and 35 grms. of potassium cyanide per litre.

(*b*) Solution for steel, wrought iron, and cast iron; 15 grms. of caustic potash, 15 grms. of stannous chloride, and 35 grms. of potassium cyanide per litre. Dissolve the caustic potash in water, add the tin chloride, then the potassium cyanide. If the tin chloride contains any iron, a precipitate will remain suspended in the solution, which should be filtered off. These solutions may be used either cold or hot. Better deposits are formed in the warm solutions. Use as large anode surface as possible, and electrolyse at tension of 2·5 to 3 volts (*Brass World*, 1911, vii., 121).

A more concentrated caustic solution than the above is said to have given very satisfactory deposits. It contained 60 grms. of soda lye, 45 grms. of fused stannous chloride, and 12 grms. of potassium cyanide per litre. Electrolysed at 1·5 volt (*Metal Industry*, 1907, v., 376).

17. J. C. Beneker obtained U.S. Patent 921,943, assigned to the Meaker Company of Chicago, for a tin electrolyte, the composition of which is 125 grms. of sodium hydroxide, 75 grms. of sodium thiosulphate, and 50 grms. of crystallised stannous chloride per litre. The solution is prepared by dissolving each of the salts separately, mixing the stannous chloride solution with the hydroxide solution, then adding the thiosulphate solution. It is stated that possibly the chief constituent of the prepared solution is sodium thiostannate (Na_2SnS). By using pure tin anodes, the deposit is produced without the formation of sponge or tree-like crystals, even when operated at high current density. The electrolyte may be used either cold or hot, but preferably hot (*Electrochemical and Metallurgical Industry*, 1909, viii., 285).

18. An electrolyte of composition similar to the Beneker solution contains 120 grms. of sodium hydroxide, 60 grms. of sodium hyposulphite, and 30 grms. of chloride of tin per litre (*Metal Industry*, 1911, ix., 90).

19. An electrolyte which is recommended to give excellent deposits of tin is prepared to contain 90 grms. of caustic soda, 15 grms. of sodium hyposulphite, 15 grms. of sodium chloride, and 30 grms. of tin chloride crystals per litre. This solution may be used either cold or hot, but gives better results when hot. Use anodes of pure tin (*Metal Industry*, 1910, viii., 87).

Conditions Necessary to Obtain Bright Dense Adherent Deposits of Tin.—The articles to be electroplated in any of these solutions must be carefully cleaned in a strong potash solution, then rubbed with lime, and subsequently thoroughly washed in clean water before placing them in the electrolyte. No time should be lost in getting the articles immersed in the plating solution directly after washing (McMillian-Cooper, "Electrometallurgy," 1910 Ed., p. 249).

There is one drawback in depositing tin from most of the baths which are in general use, namely, the anodes are not dissolved in the same ratio as tin is deposited on the cathode, consequently the strength of the bath must be kept up by the addition of a tin salt. This is best accomplished by allowing a concentrated solution of the tin salt to drip constantly into the bath during the time it is working (Watt and Phillip, "Electroplating and Electrorefining," 1911 Ed., p. 342).

Tin baths should not be used at temperatures below 20° C.; as a general rule, the higher the temperature the better the deposit.

Too high current density causes a spongy deposit, which does not adhere; whereas, with a suitable current density, a dense reguline deposit will be obtained (Langbein-Brannt, "Electrodeposition of Metals," 1909 Ed., p. 441).

W. Pfanhauser conducted a number of experiments of the formation of spongy and crystalline deposits of tin by electrolysis. He stated that the electroprecipitation of tin as thick adherent deposits is possible only in very concentrated tin-salt electrolytes, and those which contain no cations which will give rise to strongly dissociated solutions about the cathode. The best conditions for good tin deposits were found to be circulation of electrolyte, low current density, and high concentration of tin in the electrolyte. Spongy deposition is caused by poor circulation, dilute solutions, high current density, acid solutions, and impure solutions. Crystalline deposits form when the electrolyte contains no cations which are capable of forming alkali hydroxides or similar compounds, which are accompanied by the liberation of hydrogen. He used Roseleur's solution of tin chloride and sodium phosphate, and concentrated solutions of tin tetrachloride and stannous chloride (*Zeit. f. Electrochemie*, 1902, viii., 41; *Electrochemist and Metallurgist*, 1902, ii., 42; *Journ. Soc. Chem. Ind.*, 1902, xxi., 261).

In an article on "The Electrolytic Preparation of Tin Paste," the statement was made that "A spongy deposit may be due to various causes, but may be obtained nearly always by using too high a current density at the cathode. This results in an impoverishment of the electrolyte near the cathode with respect to the ions of the metal to be deposited, so that some other metal, and also generally hydrogen, is simultaneously deposited. It is under such conditions that the metal deposit becomes spongy (*Electrochemical and Metallurgical Industry*, 1905, iii., 59).

IV. *Electrolytic Refining of Tin.*

On account of the ease and comparative cheapness of refining tin by liquation methods (m.p. of tin = 232° C.) and by oxidation methods, electrolytic refining has little promise of being commercially employed.

Practically the only ore of tin is cassiterite (SnO_2; sp. gr. = 6·8 to 7·1; when pure it contains 78 per cent tin), which is found associated with such minerals as quartz, felspar, and mica in the form of granite or gneiss gangue. In some localities cassiterite is also accompanied by metalliferous minerals such as pyrite, arsenopyrite, chalcopyrite, wolframite, and molybdenite. These minerals, with the exception of wolframite, may be separated by water concentration methods. A recently developed method for separating wolframite, in case pyrite is also present, consists in calcining to the magnetic condition, then subjecting the pulverised ore to magnetic separation, the pyrite and the wolframite being removed (Schnabel-Louis, "Handbook of Metallurgy," II., 1907 Ed., p. 478; Louis, "Metallurgy of Tin," 1911 Ed., p. 12).

Commercial tin contains from 0·5 to 1·5 per cent of impurity, which is one or more of the following metals:—Zinc, iron, lead, bismuth, antimony, copper, arsenic, tungsten, molybdenum, silver. As there is no demand for very pure tin, and also because silver and gold are not present in quantity to pay for their recovery, electrolytic refining has, up to the present time, not been practised, except when very pure metal was wanted or when experimental refining was conducted. The product which is produced by pyro-heat methods of refining is of sufficient purity for commercial purposes.

A number of electrolytic methods have been developed, the majority using electrolytes of the stannous salt. The efficiency of the refining is given for some of the electrolytes, the figures being obtained by using the factors for stannous solutions which are 0·6163 mgrm. per coulomb,

2·2188 grms. per ampère-hour, 204·43 ampère-hours per pound; the factors for stannic solutions are 0·30817 mgrm. per coulomb, 1·1094 grm. per ampère-hour, 408·86 ampère-hours per pound.

1. Brand conducted experiments on the electrolytic refining of tin, using an electrolyte containing 2·5 per cent by volume of concentrated hydrochloric acid and 9 per cent by weight of stannous chloride. The method did not find commercial application (Schnabel-Louis, "Handbook of Metallurgy," 1907 Ed., II., p. 549; Dammer, *Chem. Technology*, ii., 27, 324).

2. Michaud and Delasson received French Patent 435,936 for the use of a tin electrolyte prepared by dissolving stannous chloride in water, adding sulphuric acid till the precipitated oxychloride dissolved, and then stirring into the solution about 1 per cent of magnesium chloride and 1 per cent of boric acid. The cell used for the refining is constructed with a sheet copper cathode placed horizontally on the bottom, on which the tin crystals are deposited and removed by scrapers (*Journ. Soc. Chem. Ind.*, 1912, xxxi., 395).

3. Mennicke conducted experiments on the electrolytic refining of tin in fluosilicate electrolytes, and obtained deposits which were similar to lead deposits produced under the same conditions of current-density and temperature. The electrolyte was prepared by dissolving freshly precipitated stannous hydroxide in hydrofluosilicic acid in proper proportions to give a solution containing 10 per cent free hydrofluosilicic acid by weight. Tin oxide was found to be insoluble in hydrofluosilic acid. The presence of free hydrofluoric acid was found not to interfere with the production of satisfactory deposits.

The electrolysis was conducted at 20° C., using current at density of 9·3 ampère per sq. ft. (1 amp. per sq. dm.) and an average of 0·4 volt. Distance between electrodes about 2 inches (5 cm.). The tin deposited extremely solid and tough, even without the presence of any addition-agent such as gelatin or albumen. The lower the voltage the finer the crystals.

Better results were obtained by using pure tin anodes than with those of a tin alloy. The presence of lead finally caused the deposit to become spongy, but still the deposited tin was pure. He states that very pure tin can be produced, which is especially suited for preparing pure chemicals (*Electrochem. Zeit.*, 1905, cxii., 135, 161, and 180; *Zeit. f. Electro. Chem.*, xii., 112; *Electrochem. and Metallurgical Ind.*, iv., 26; *Mineral Industry*, xiv., 555; Betts, "Lead Refining by Electrolysis," 1908, p. 47).

4. Mention has been made that neutral concentrated solutions of either stannic chloride or stannous chloride can be used for producing pure tin, as these electrolytes yield a coarse crystalline deposit (Neumann-Kershaw, "Electrolytic Methods of Analysis," 1898 Ed., p. 148).

5. Beautiful dense deposits of tin can be produced without the evolution of hydrogen at the cathode by electrolysing a solution of sodium-stannous chloride with low current-density and at ordinary temperature (*Bull. Soc. d'Enc. L'Ind. Nat.*, July, 1912, p. 28).

6. Quintane was granted English Patent 5496 for the deposition of pure tin by use of an electrolyte composed of stannic chloride, or stannous chloride, and an ammoniacal salt, preferably ammonium chloride. It is claimed that a perfect deposit of chemically pure tin was produced from this solution. The statement is made that "to obtain a clear solution, and one that will act as a good conductor of the current, the precipitate first formed on dissolving the tin salt in water is re-dissolved by the addition of ammonium chloride, and the solution filtered. The current should be weaker than that employed for the electrodeposition of copper, or the deposit will be irregular" (*Journ. Soc. Chem. Ind.*, 1900, xix., 1121; *Mineral Ind.*, ix., 646).

7. Hollard prevented the formation of spongy deposits of tin by using an electrolyte composed of 12 grms. of sodium stannate (Na_2SnO_3) and 200 grms. of sodium sulphate per litre, and electrolysing it at a temperature of 80° C. at current-density of 2 ampères per sq. ft. (0·2 amp. per sq. dm.) (*Bull. Soc. d'Enc. Ind. Nat.*, July, 1912, p. 28).

8. Fischer satisfactorily deposited tin by using a solution of ammonium sulpho-stannate to which was added a reducing agent such as sodium sulphite, sodium hyposulphite, or potassium cyanide (*Zeit. Anorg. Chem.*, 1904, xlii., 363).

9. Neumann received German Patent 198,289 for a process of obtaining pure dense deposits of tin by use of an electrolyte composed of an alkali sulpho-stannate, and operating at temperature of about 70° C. The presence of free alkali is said to be advantageous.

10. Claus refined tin in an aqueous solution of sodium sulpho-stannate, of sp. gr. 1·07, and at 90° C., employing current at 10 ampères per sq. ft. (0·9 amp. per sq. dm.). All the impurities except arsenic and antimony collected as anode sludge, principally as sulphides. Arsenic and antimony, when present, were precipitated on the cathode with the tin. He found that the cathode tin containing arsenic and antimony could be freed from these by making it an anode in an acid solution of sodium thiosulphate containing hydrochloric acid, the arsenic and antimony in this case remaining as sulphides in the anode sludge. The cathode tin was melted and cast into bars (*Electrochem. Zeit.*, viii., 168; Schnabel-Louis, "Handbook of Metallurgy," 1907 Ed., xi., 549).

11. Patents have been granted to O. Steiner for a tin refining process, using an electrolyte similar to that published by Claus, as given above (10). The patents issued are:—U.S. Patent 890,249; German Patent 193,528; English Patent 10,230; French Patent 374,116. The claims are that by using an electrolyte containing about 10 per cent by weight of an alkali sulphide, to which has been added about 1 per cent by weight of flowers of sulphur, tin of high purity (99·9 per cent) could be produced as a dense smooth deposit, when the electrolysis is conducted so that the E.M.F. is kept below 0·2 volt, current-density under 4·5 ampères per sq. ft., and solution kept at about 90° C.

The electrolyte is prepared by dissolving commercial sodium sulphide in the necessary amount of water to produce a 10 per cent solution, adding 1 per cent by weight of flowers of sulphur, letting settle, then filtering. It is necessary to analyse the solution at intervals during the electrolysis, and to add sodium sulphide and flowers of sulphur so as to keep up the concentration. The loss of sodium sulphide will be due to oxidation and to the formation of sodium sulpho stannate. The amount of tin in the electrolyte reaches a maximum of about 2·2 per cent by weight, and remains constant thereafter so long as the concentration of sodium sulphide is kept proper.

One of the essentials in the use of this solution for refining tin is that the voltage must be kept below 0·2, and that the electrolyte be maintained above 90° C. If the potential is allowed to rise, gassing at the cathode occurs. At 0·6 volt violent liberation of hydrogen takes place, with decomposition of the electrolyte, and at the same time the tin deposits as a dull spongy mass which contains oxide.

The raw tin should not contain more than 10 per cent of impurities, and the iron content should be below 2 per cent, otherwise the anode sludge will adhere and cause the voltage to rise and produce gassing and a spongy deposit. The anode sludge will contain the iron, lead, antimony, copper, bismuth, and silver. Distance between the electrodes about 1⅜ in. (3·5 cm.). Iron tanks are most suitable.

The conditions which are given as being necessary to obtain high current efficiency and to produce dense pure deposits are:—

(*a*) Temperature of electrolyte above 90° C.

(*b*) Thorough and constant circulation, or mixing of electrolyte.

(*c*) Voltage maintained below 0·2.

(*d*) Pure plate cathodes (cathodes of iron, copper, and lead cause the voltage to rise and the deposit to be non-adherent and spongy).

(*e*) Pure electrolytes, free of arsenic, antimony, copper, &c.

(*f*) Electrolyte containing 10 or more per cent of sodium sulphide by weight. A more concentrated solution permits the use of higher current-density.

(*g*) Add to the electrolyte about 1 per cent by weight of flowers of sulphur just before placing a new lot of anodes in the tank. The sulphur is necessary to form sulphides with the impurities in the anode, thereby preventing the contamination of the electrolyte.

(*h*) The electrolysis must not be interrupted until the anodes are to be removed. When the current is interrupted, gassing will occur when the current is switched on, and spongy deposit will form.

A means of maintaining the same current-density from a number of electrodes when placed in the same tank, was accomplished by soldering all of the anodes to the same supply conductor and all of the cathodes to the negative conductor. When this was not done the voltage between all of the opposite electrodes was not the same.

The ampère-hour efficiency is given as above, 98·5 per cent. It is also stated that "the deposit could be still improved by adding a colloid to the electrolyte, for example, gelatin as is used in the Betts' process for electrolytically refining lead" (*Electrochem. Zeit.*, May, 1908; *Journ. Soc. Chem. Ind.*, 1907, xxvi., 768; *Electrochem. and Metallurgical Ind.*, 1907, v., 309).

12. Sperry obtained U.S. Patent 874,707 for a process of refining tin by the use of a diaphragm cell. It is stated that electrolytes consisting either of sulphate, ammonium oxalate, ammonium sulphide, or of chloride, fluoride, or hydrofluoric acid could be used in the cell. The impure metal to be electrolytically refined may be given a preliminary refining by fire-methods in order to remove the major portion of the impurities, then cast into anodes. The use of the diaphragm between the anodes and the cathodes is to prevent the cathode deposit becoming contaminated by floating anode sludge. The impurities which accumulate in the electrolyte as soluble salts are to be removed periodically by withdrawal of a portion of the electrolyte, and replacing it by fresh solution. Electrolytes work better when kept at 85° C. (*Journ. Soc. Chem. Ind.*, xxvii., 343; *Electrochem. and Metallurgical Ind.*, vi., 76).

There are several articles, in themselves reviews, which could not be reviewed. They may be found in the following publications:—

Electrical Engineering, London, July 15, 1898, "The Electrolytic Refining of Tin and Recovery of Tin from its Ores," by Sherard Cowper-Coles.

Electrochem. Zeit., Berlin, March, 1907, "Recent Progress in the Metallurgy of Tin, with Regard to Electrochemistry in 1906," by H. Mennicke.

Electrochem. Zeit., Berlin, July, 1908, "Progress in the Metallurgy of Tin with Special Reference to Electrochemistry in 1907," by H. Mennicke.

Electrochem. Zeit., Berlin, January, 1910, "Electrolytic Precipitation of Tin," by B. Pasztor.

(To be continued).

NOTICES OF BOOKS.

A Text-book on Trade Waste Waters: Their Nature and Disposal. By H. MACLEAN WILSON, M.D., B.Sc., and H. T. CALVERT, M.Sc., Ph.D., F.I.C. London: Charles Griffin and Co., Ltd. 1913.

IN this book the nature and disposal of the waste liquids of the important industries are discussed in great detail. The coal trade, gas manufacture, brewing, leather, paper, and textile trades are considered in turn, the latter being given specially full treatment, and in each case the most important practical methods of treating the liquid refuse are described, with plans and diagrams of the necessary plant and full statistics as to cost of working and efficiency. The advice given to manufacturers regarding choice of methods, the necessity for constant analyses and for the correct estimation of the volume of the refuse is always thoroughly practical, and the results of many years of experience of the working of the Rivers Pollution Prevention Acts are embodied in the book. An excellent outline of the methods usually employed in the analysis of waste waters is included.

Jahrbuch der Elektrochemie und Angewandten Physikalischen Chemie. Berichte uber die Fortschritte des Jahres 1906. ("Year Book of Electrochemistry and Applied Physical Chemistry. Reports of Advances in the Year 1906." Edited by Dr. phil. HEINRICH DANNEEL and Prof. Dr. JULIUS MEYER. Vol. XIII. Halle (Saale): Wilhelm Knapp. 1913. (M. 32).

THIS year-book is divided into two sections, the first and longer of which treats of the developments of the scientific side of the subject, while in the second part the applications of electrochemistry are considered. The treatment is very comprehensive and thoroughly systematic; no very important discoveries have to be recorded, but, on the other hand, general advances have been made in all branches. It is greatly to be regretted that it has not been found possible to issue Volume XIII. of the year-book somewhat earlier; in the last seven years the growth of the subject has been rapid, and much that was published in 1906 must now be regarded as out of date.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clvi., No. 21, May 26, 1913.

Action of Ammonia on Monoethylamine.—Félix Bidet.—The author has already shown that the action of ammonia on the hydrochlorides of amylamine and ethylene diamine constitutes a chemical equilibrium. The study of the action of the gas upon solid anhydrous monoethylamine hydrochloride shows that the velocity of the reaction is greater than with the other hydrochlorides. It decreases appreciably as the pressure of the ammonia diminishes. The velocity is greater for the inverse than for the direct reaction.

Instability of Ferric Fluosilicate.—A. Recoura.—Berzelius stated that ferric fluosilicate could be obtained as a gummy semi-transparent mass by saturating fluosilic acid with ferric hydrate and evaporating the solution. The author's experiments prove, however, that ferric fluosilicate does not exist, and when attempts are made to prepare it either by Berzelius's method or by double decomposition it immediately splits up into another more stable double fluoride, losing one-third of its silicon fluoride, $(SiF_4)_3Fe_2F_6 = SiF_4 + (SiF_4)_2.Fe_2F_6$.

Ether Salts Derived from Octanol-2.—J. B. Senderens and J. Aboulenc.—By keeping a mixture of octanol-2 (one molecule) and organic acid (1·05 mol.) at a temperature not exceeding 100° ether salts can be obtained, if 2 to 3 per cent of H_2SO_4 is added as a catalyst. Sulphuric acid does not act as a catalyst towards those aromatic acids in which the carboxyl is directly united to the radicle, but if the carboxyl is separated by a chain, as in phenylacetic acid, it brings about catalytic etherification.

Condensation of Primary and Secondary Aromatic Amines with Mesoxalic Ethers.—A. Guyot and J. Martinet.—The condensation of primary amines, such as monoethylaniline with ethyl mesoxalate, is readily effected,

the principal product being a dioxindol-3-carbonic ether, while a small quantity of phenyl tartronic ether is also formed. The former ether is readily saponified by means of aqueous potash, the corresponding dioxindol being obtained. The saponification has to be carried out in absence of air, otherwise the alkaline solution absorbs oxygen and the dioxindol is transformed quantitatively into isatine.

Action of a-Monochlorhydrine and Epichlorhydrine upon Monosodium Glycerin.—Jean Nivière.—When monosodium glycerin reacts on α-monochlorhydrine glycide is the principal product, some diglyceric alcohol being also obtained. With epichlorhydrine a polymer of the anhydride of diglyceric alcohol is formed. It is a white amorphous substance insoluble in water, alcohol, ether, pyridine, and nitrobenzene. When boiled with acetic anhydride in presence of fused sodium acetate it gives a diacetyl derivative. Both substances decompose when heated without undergoing decomposition.

Properties of Carbon Tetraiodide and its Estimation in presence of Iodoform.—Marcel Lantenois.—Tetraiodide of carbon is decomposed quantitatively even in the dark by pure oxygen, iodine being liberated and carbon oxyiodide formed. The oxyiodide is unstable, and the gases formed during the reaction also contain carbon monoxide and a small proportion of carbon dioxide. The action is facilitated by light. In atmospheric air the transformation is less rapid. Carbon iodide reacts with a certain number of metalloidal chlorine compounds to give the corresponding iodide and a chloroiodide of carbon. When carbon iodide reacts with silver nitrate the two following equations appear to take place simultaneously:—

$$CI_4+4AgNO_3+2H_2O=CO_2+4HNO_3+4AgI,$$
$$3CI_4+12AgNO_3+6H_2O=3CO+AgIO_3+11AgI+12HNO_3.$$

Each of these reactions gives a molecule of gas for a molecule of tetraiodide. Hence whatever the proportions of the two oxides of carbon the volume of their mixture bears a definite relation to the weight of iodide. This reaction can be applied to estimate the tetraiodide in presence of iodoform. The volume of gas obtained is 42·9 cc. for 1 grm. of tetraiodide, and 56·6 cc. for 1 grm. of iodoform, and the two gases can be measured with great accuracy.

MISCELLANEOUS.

City and Guilds of London Institute.—On the report of the Delegacy of the City and Guilds (Engineering) College, the Council of the City and Guilds of London Institute have awarded the Diploma of "Associate of the Institute" to the following matriculated third year students who have completed a full course of instruction as prescribed by the Council. (An asterisk denotes entered as a second-year student):—*Civil and Mechanical Engineering* (57 out of 90)—O. B. Binns* (Bramwell Medal), W. H. Thomas (Henrici Medal), A. Singh Sarkaria, W. Collins, G. L. Groves, A. E. Walker, F. G. D. Stoney, E. Robinson,* F. J. G. Foot, C. W. J. Taffs,* F. White,* F. Buckingham,* Q. Z. Huzain, E. S. May, Anokh Singh,* W. R. Sheffield, J. W. Bansall,* J. T. Down, J. M. Boyd, I. Edeleanu, R. H. Paddison, K. L. Nanda, A. M. R. Montagu,* J. N. Nanda, H. W. L. Poole, S. E. M. Firth, L. A. Ritchie, J. A. Mercer,* E. L. Wildy, W. M. Carmichael, F. H. Hutchinson, C. T. W. Sauerbeck, P. V. Hoare,* J. H. Fletcher, E. F. Elderton, M. D. Wilicock,* K. Singh, M. Fatehullah, S. P. Hannam, D. Milner,* E. Ramirez, G. E. Gill, J. S. Roberts, F. R. Roberts, J. H. Saint, P. R. Purves, L. L. Vigers, E. G. Timbrell,* R. G. Cleveland, J. D. Davies, H. D. D. Smith, F. L. Richards, C. G. Whitmore,* E. A. P. Wood, O. Hodgson,* F. D. Napier-Clavering, G. C. Totton. *Electrical Engineering* (21 out of 27)—E. A. Richards (Siemens Memorial Medal), R. S. H. Boulding* (Siemens Memorial Medal), D. Dunham, G. J. Websdale, D. H. Linsley, N. H. Barker,* U. Singh, L. B. Hobgen, L. G. Floyd, H. B. Lee, A. G. C. Holroyde, V. H. G. Parker, J. C. Elmer,* R. C. Wrinch, J. P. Clifton, H. A. Denison, W. Ryley, N. D. Edingborough, A. H. Hall, P. Jackson,* H. Singh Siddhù. *Chemistry* (6 out of 8)—A. W. Long, E. Watson, C. E. M. Richards, D. W. C. West,* N. J. Read, K. Hooper.

University of London.—*Appointments Board.*—The Appointments Board, constituted by the Senate to assist Graduates and Students of the University in obtaining appointments, and to co-ordinate and supplement the work done by the Schools and Institutions of the University in this direction, registers the qualifications of: (*a*) Graduates of the University of London; (*b*) Graduates of other Universities who are students of London; (*c*) Undergraduates in their last term, previous to entry on Degree Examinations. The fee for registration has for the present been fixed at 5s., renewable annually so long as the name is retained on the registers. The Board reported to the Senate in June, that since the appointment of a full-time Secretary the work of the Board had increased to a very considerable extent. The Secretary had visited permanent officials of many Government Departments, and received promises of support in the work of the Board; he had also visited the officials of the Oxford and Cambridge Appointments Board, the Teachers' Registration Council, and a number of Principals, Headmasters, Headmistresses, and Secretaries of Educational Organisations. The London Chamber of Commerce, the Association of University Women Teachers, the Central Bureau for the Employment of Women, and various Colleges and Schools had expressed their readiness and desire to co-operate with the Board. Upwards of 200 graduates and stedents had visited the Secretary—many to seek specific advice. The Secretary (Dr. A. D. Denning) will be pleased to give further information, and to see graduates at the Central Offices of the University, South Kensington (Room 23) on Wednesday afternoons, 2 to 5, or Thursdays, 12 to 1.30, or at other times by arrangement. Educational Authorities, Business Firms, and others, having openings for Graduates, are asked to inform the Secretary, who will forthwith notify the more suitable available Graduates on his registers, and use every endeavour to secure the candidature of the most capable applicants. Approximately 1000 posts have been notified to suitably qualified graduates registered with the Board within the last three months and many appointments secured. Further registrations of well-qualified graduates and students are now necessary.

Uses of Cast Silicon.—According to *Metallurgical and Chemical Engineering*, xi., 103, silicon is used in the form of pipes for the conveyance of acid gases at a high temperature from stills to condensers, also in the construction of the condensing batteries themselves, proving more efficient than stoneware owing to its high thermal conductivity and ability to withstand sudden changes of temperature. Silicon pipes are also used for the transportation of hot liquid sulphuric and nitric acids, but it cannot be used for hydrochloric acid unless the discoloration resulting from the slight solubility is immaterial. It is used as a lining in centrifugal pumps, acid valves, and pipes for the elevation of corrosive liquids by compressed air, and for the construction of ploughs in ore roasters it is said to have proven efficient. Cast silicon is also being employed in the form of shallow pans and pots for the concentration of zinc chloride solutions, supplanting the enamelled stoneware vessels which are rapidly destroyed. Cast silicon ware is said to be produced in practically all shapes required by the chemical industries, such as, for example, pipes, evaporating vessels, receivers, tiles, alembics, crucibles, and pump parts.—*Journal of Industrial and Engineering Chemistry*, v., No. 3.

THE CHEMICAL NEWS.

VOL. CVIII., No. 2803.

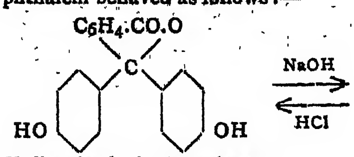
CRITICISM OF A RECENT CONTRIBUTION TO THE THEORY OF INDICATORS.

By ARTHUR G. A. MILLER, B.Sc. (Lond.), F.C.S.

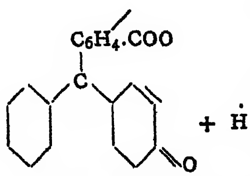
IN a recent contribution to the theory of indicators (Dr. J. Waddell, CHEMICAL NEWS, 1913, cvii., 206), the author states that, according to the ordinary theory of indicators, it is strange that methyl-orange, a strong acid, should act towards weak acids, as phenolphthalein, a weak acid, acts towards weak bases, and that the anomaly is removed if methyl-orange is considered to be a weak base instead of a strong acid.

The author appears to have based his conclusion upon purely physico chemical considerations, without having due regard to the question of the chemical constitution of the indicator, which is now generally admitted to play a most important part. Indeed, many chemists are strongly of the opinion that the two views are complementary, and experimental evidence seems to confirm this. Indicators are now regarded, not as a true, but as *pseudo* acids or bases (so-called by Hantzsch), and that the undissociated molecule is really a mixture of one or more tautomeric forms in equilibrium, only one of which ionises to a considerable extent (see H. T. Tizard, *B.A. Reports*, 1911, p. 268).

Thus, on the old theory, it was considered that phenolphthalein behaved as follows:—

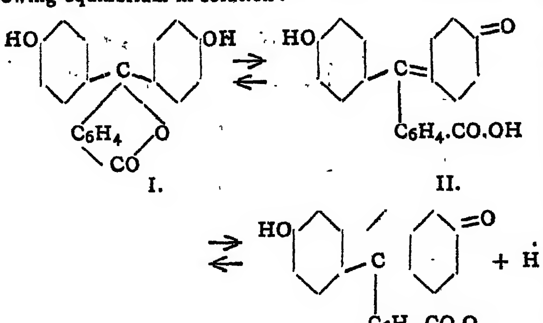


Undissociated colourless substance (lactone).



Coloured quinonoid ion.

At the present time it is considered as showing the following equilibrium in solution:—



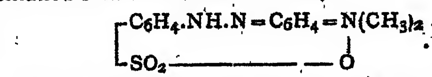
Coloured ion.

Configuration I. is the more stable, and the acid is very weak; hence, Configuration II. and its ions are only present to a very small extent in the solution, which in consequence is colourless. Addition of bases (hydroxyl ions) diminishes the concentration of hydrogen ions to such an extent that the colour due to Configuration II. makes its appearance. Consider the case quoted by the author, of the removal of the colour produced by the action of concentrated ammonia solution on phenolphthaleïn, by the addition of ammonium salts such as ammonium chloride. As is well known, ammonia solution contains hydroxyl ions in relatively small amount. Applying the law of mass action, any addition of ammonium salts (ammonium ions) must diminish the concentration of hydroxyl ions in order to preserve equilibrium, and with corresponding increase of hydrogen ion concentration Configuration I. becomes the stable one; that is, the solution becomes colourless. Chemical evidence is not lacking in support of the statement that tautomerism exists. In the case of phenolphthaleïn the red colour is destroyed on the addition of alcohol or acetone, and this is undoubtedly due to ionisation change. On the other hand, the dry salts of the indicator are red, and, further, a coloured quinonoïd carboxylic methyl ester has been isolated; in these cases there can be clearly no question of ionisation. Both explanations are thus accounted for in dealing with the colour change of phenolphthaleïn.

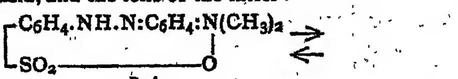
Coming now to the case of an amphoteric indicator (*i.e.*, one which has both acidic and basic groupings in the molecule) such as methyl-orange, its sodium salt,—

$$NaSO_3C_6H_4N = NC_6H_4N(CH_3)_2,$$

is yellow, while the free acid is violet. It seemed very probable that the strongly acidic sulphonic group was modified by the basic aminic group, and accordingly Hewitt (*Analyst*, 1908, xxxiii., 85) assigned to the free acid in the solid condition, or in acid solution, the constitution of an internal salt. Thus,—



This view was put forward about the same time independently by Hantzsch (*Ber.*, 1908, xli., 1187). Thus the aqueous solution consists of an equilibrium mixture of the internal salt, the true dimethylaminoazobenzene sulphonic acid, and the ions of the latter:—



Red.

$$HSO_3.C_6H_4N:NC_6H_4N(CH_3)_2 \rightleftarrows$$

Yellow.

$$\dot{H} + SO_3.C_6H_4N':NC_6H_4.N(CH_3)_2$$

Yellow.

Addition of hydrogen ions will diminish the dissociation and produce the internal quinonoïd configuration, while, on the other hand, the addition of even a weak base will remove hydrogen ions, and the yellow colour due to the azoïd ions will appear. There is, again, chemical evidence for the assumption that tautomerism exists in this case. Thus the sodium salt of methyl-orange has the well-known orange-yellow colour, and it has been shown that the dry silver salt has the same violet colour as the free "acid." Clearly here there is no case of ionic dissociation, and it is naturally concluded that the free acid of methyl-orange can exist in tautomeric forms.

One has now to explain the behaviour of methyl orange to a weak acid such as acetic acid. Consider an indicator which is a weak acid (methyl orange is relatively weak in comparison with a strong mineral acid), and let its degree of ionisation in solution be α. Appling Ostwald's law of dilution one has—

K × concentration of undissociated molecules = concentration of dissociated molecules × concentration of hydrogen ions,

or—

$$K \times \frac{1-\alpha}{\alpha} = \text{concentration of hydrogen ions;}$$

where K is the dissociation constant of the indicator. The degree of ionisation of an indicator, and therefore of its colour, thus depends upon the constant K and the concentration of hydrogen ions in the solution. Thus for every indicator there is a particular concentration of hydrogen ions necessary to produce a colour change (see Salm, *Zeit. Phys. Chem.*, 1906, lvii., 471). For methyl-orange the concentration of hydrogen ions lies between 10^{-3} and 10^{-4} normal. Evidently there is such a concentration of hydrogen ions present in a weak acid like acetic acid, but it is very easily diminished by the addition of acetone, alcohol, or acetates, so that the now unstable red internal quinonoïd configuration gives place to the stable tautomeric azoïd form, which at once ionises with the production of the well-known yellow ion.

Dr. Waddell points out that the sulphonic group is strongly acidic, but acting against this is the aminic group, conferring a basic character which is accentuated in the sodium compound. There is, however, no doubt that the acidic character of the molecule predominates. At the same time, it is believed that the basic character of the aminic group very largely influences the sensitiveness of the indicator to hydrogen ions. Thus dimethyl-α-naphthylamine is more basic in character than dimethylaniline, and the author of this communication found that an indicator prepared by coupling the former substance with diazotised sulphanilic acid was more sensitive to hydrogen ions than methyl-orange. On the other hand, diphenylamine is almost non-basic in character, and the azo-compound made by coupling it with diazotised sulphanilic acid was found to require a considerable concentration of hydrogen ions to effect a noticeable colour change.

Finally, Dr. Waddell stated that he believed if almost dry hydrochloric acid was passed into an alcoholic solution of methyl orange the colour of the solution would still remain yellow. The experiment has been carried out using a solution of methyl-orange in absolute alcohol; but there was an immediate red coloration produced owing to the fact that hydrochloric acid, one of the strongest acids, can exert its power of ionisation even in the presence of absolute alcohol.

Thus it seems as if the theory of indicators accepted at the present time is in complete accord with the behaviour of methyl-orange, and that Dr. Waddell's views regarding the yellow sodium salt of methyl-orange as being undissociated in solution, and the red colour produced by the addition of acids is due to the dissociated cation are untenable.

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PRELIMINARY NOTE ON A NEW METHOD FOR THE DIRECT DETERMINATION OF RUBBER.*

By L. G. WESSON.

The chief difficulty that has stood in the way of the direct determination of rubber has been the uncertain composition of the derivatives, such as the tetrabromide and nitro compounds, used in the methods proposed up to date. This has suggested a method which avoids this source of error by forming a derivative, the nitrosite, whose composition is immaterial so long as it contains all the carbon which belonged to the rubber of the sample under analysis. On analysing this derivative for carbon, we are then enabled to calculate how much rubber the derivative represents.

The procedure, in brief, consists in allowing the acetone-extracted sample to dissolve or swell up in carbon tetrachloride, after which nitrous gases, evolved by dropping HNO_3 on As_2O_3, form the nitrosite of rubber by passing through the solution to saturation. After standing, the now soluble nitrosite is dissolved in acetone, from which it is obtained in a form ready for combustion by a method of precipitation or evaporation. The details of both of these methods are being studied to eliminate known sources of error and to further simplify the manipulation.

The tediousness of the latter has been considerably relieved by the development of a durable electric organic combustion furnace adapted for this work. It consists of a tube of Jena glass 60 cm. long and 2¼ cm. bore, containing a coil of electrically heated platinum wire, and a boat of lead peroxide and minium heated by an external coil of nichrome wire. Two heavy copper wires, coated with iridium and pushed through the one-holed rubber stopper at the forward end of the tube, solve, in a convenient manner, the problem of making an external contact for the useful directly heated catalyser coil. The leads for the coil simply rest on the hooked ends of these wires, thus permitting an easy removal and replacement of the stopper, the coil, or the lead peroxide boat which rests between the coil and the stopper. It is thought that, with a few modifications, this form of furnace is adapted for general organic combustions, and it will be tested soon with that end in view.

The use of the lead peroxide boat which absorbs the sulphur of the nitrosite as lead sulphate, should give a means for the estimation of the sulphur of vulcanisation; if, as Alexander emphatically asserts (*Ber.*, xl., 1077; *Zeit. Angew. Chem.*, xx., 1364; xxiv., 687), the sulphur combined with the rubber is carried quantitatively into its nitrosite.

The following figures have been obtained by the use of either the precipitation or evaporation methods:—

A washed and dried fine para, precipitated once from chloroform, dried to constant weight in hydrogen at 92°, and analysed as 99·1 per cent carbon plus hydrogen, gave 99·5, 98·7, 97·8, 98·0, 97·1, and 96·6 per cent $C_{10}H_{16}$.

A washed and dried fine para gave 95·7, 94·7, 94·8, 95·2, and 95·5 per cent $C_{10}H_{16}$.

A rubber compound containing litharge, whiting, barytes, zinc oxide, sulphur, and 48 per cent para, or 45·4 per cent rubber, gave 45·3, 46·4, 48·7, 47·2, and 45·6 per cent $C_{10}H_{16}$.

Another containing the same ingredients with the addition of paraffin, with 28·6 per cent fine para or 27·8 per cent rubber, gave 27·5, 27·4, 27·7, 26·7, 27·1, and 26·9 per cent $C_{10}H_{16}$.

These results, however, represent only those that have been obtained under the best conditions, and are not subject to the numerous sources of error that have continually appeared. They seem to be of sufficient value to justify putting on record at this time. Further work should give a greater reliability and accuracy, in which case full details of the method and apparatus will be published.

* Paper presented at the Annual Meeting of the American Chemical Society, Milwaukee, March, 1913. (Published by permission of the Director of the Bureau of Standards). From *Journal of Industrial and Engineering Chemistry*, v., No. 5.

POTASSIUM PERMANGANATE IN THE QUANTITATIVE ESTIMATION OF SOME ORGANIC COMPOUNDS.*

By C. M. PENCE.

Potassium permanganate has been most generally used in the volumetric estimation of iron. Some uncertainties formerly existed since it was impossible to obtain a chemically pure article, and insufficient data were at hand as to proper methods of preparation and standardisation of its solutions.

At present these objections have been largely overcome, and almost all of our text-books on quantitative analysis contain an extended treatise on proper means of preparation and standardisation of volumetric permanganate solutions.

* Read before the Indiana Section of the American Chemical Society. From the *Journal of Industrial and Engineering Chemistry*, v., No. 3.

One of the most commonly known organic compounds that is quantitatively determined by the use of volumetric permanganate is oxalic acid. Now oxalic acid and iron are determined in acid solution, but the procedure most applicable for the oxidation of all types of aromatic compounds as well as carbohydrates and hydrocarbons is with alkaline permanganate. Oxidations in acid solution are less energetic than those with alkaline $KMnO_4$, and in the latter case the final product of a completed decomposition of the organic compound is oxalic acid instead of CO_2 and H_2O.

Among the substances mentioned in the literature (see Note) as being oxidised to oxalic acid are propylene, isobutylene, amylene, acetone, fatty acids; butyric, lactic, succinic, and tartaric acids; dextrose, sucrose, glycerol, and phenol. Now when an organic compound is oxidised to oxalic acid, a further oxidation to CO_2 and H_2O readily follows upon acidifying and warming the solution. Such a procedure forms the nucleus of a method for the determination of the compounds previously enumerated. Tocher made use of this method, and found that phenol could be determined. His method was substantially as follows:—Dissolve 1 grm. phenol in 1000 cc. distilled water, and take 10 cc. for titration. Add 3 to 4 grms. $NaHCO_3$ together with a little distilled water. Then add 50 cc. $KMnO_4$, and boil for five minutes. Set aside to cool, and gradually add dilute H_2SO_4 to decided excess; warm to 60° C., and titrate the excess of N/10 $KMnO_4$ with N/10 oxalic acid.

(Note.—"Oxidation of organic Compounds with Alkaline Permanganate," Eduard Donath and Hugo Ditz, *Journ. Prakt. Chem.*, 1899, [2], lx., 566; through *Journ. Chem. Soc.*, 1900, [1], lxxviii., 197; "Contribution to the Knowledge and Determination of the Carbohydrates,"-J. König, W. Greifenhagen, and A. Scholl, *Zeit. Nahr. Genussm.*, xxii., 705; through Abstr. *Journ. Am. Chem. Soc.*, 1912, vi., 901; "Volumetric Determination of Phenol," Jas. F. Tocher, *Pharm. Journ.*, lxvi., 360).

This method was found to be open to the following objection:—That the manganese dioxide formed as a result of the action of N/10 $KMnO_4$ upon the phenol did not reduce readily enough with consequent solution upon direct titration with N/10 oxalic acid. Thus the solution was full of oxide which not only obscured but rendered the end-point of little value, in that the oxide was not completely reduced before the permanganate end-point was obtained.

The following modification of Tocher's method was found to give good results:—

Dissolve 0·4 grm. phenol in 1000 cc. distilled water. Place 50 cc. N/10 $KMnO_4$ and 3 to 4 grms. $NaHCO_3$ in a 500 cc. glass-stoppered Erlenmeyer flask. Add 25 cc. of the phenol solution with gentle rotation. Boil five to ten minutes (with stopper removed). Cool flask to about 60° C. Acidify with dilute H_2SO_4, let stand about two minutes; cool to room temperature. Dilute with distilled water, add 5 cc. 20 per cent KI, and titrate the liberated iodine with N/10 thiosulphate solution, using starch as indicator. The number of cc. of N/10 thiosulphate subtracted from the number of cc. $KMnO_4$ originally added = No. cc. of $KMnO_4$ consumed by the phenol.

1 cc. N/10 $KMnO_4$ = 0·000336 grm. phenol.

If a glass-stoppered Erlenmeyer flask is not available an ordinary Erlenmeyer may be used, and its contents transferred to a glass-stoppered bottle before acidifying. Any oxide adhering to the Erlenmeyer is easily removed by the addition of a little distilled water acidified with H_2SO_4, and containing a few drops of 20 per cent KI.

In considering the nature of the oxidation with $KMnO_4$ in acid and alkaline solutions it is observed that each molecule of $KMnO_4$ in acid solution liberates 2·5 atoms of oxygen according to the following equation:—

$$2KMnO_4 = K_2O + 2MnO + 5O,$$

or—

$$2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 3H_2O + 5O.$$

Now in alkaline solutions the two molecules of MnO are immediately oxidised to $2MnO_2$ at the expense of 2 atoms of oxygen, so that we actually have $2KMnO_4 = K_2O \cdot 2MnO_2 + 3O$. Hence, for each molecule of $KMnO_4$ used, only $1\frac{1}{2}$ atoms of oxygen are available for our oxidation process. This fact must be recognised in providing sufficient $KMnO_4$ to readily complete the oxidation process, and it would necessarily enter into a calculation of the value of N/10 $KMnO_4$ in terms of phenol if the MnO_2, or rather its hydrated form, were filtered from the solution before acidifying and adding the KI. But since the procedure is not lengthened by a filtration the MnO_2 is reduced to its manganous form with the liberation of free iodine, and we must calculate our factor by considering that reaction proceeds as in acid solution with 2·5 atoms of oxygen available per molecule of $KMnO_4$, although such is not literally the truth.

To completely oxidise phenol, 14 atoms of oxygen are required, according to the following equation:—$C_6H_5OH + 14O = 6CO_2 + 3H_2O$. Since only 2·5 atoms of oxygen are available per molecule of $KMnO_4$ then 5·6 molecules of $KMnO_4$ would be required for every molecule of phenol, and the factor for N/10 $KMnO_4$ in terms of phenol becomes:—

$$\frac{\text{Mol. wt. phenol}}{2\cdot5 \times 2 \times 10 \times 5\cdot6 \times 1000}.$$

Experiments with a phenol solution containing 0·0005 grm. of phenol per cc., as determined by the Koppeschaar bromine method, resulted as follows:—

Ex. No.	Grm. phenol taken.	Per cent phenol found.
1.	0·0050	99·65
2.	0·0050	100·18
3.	0·0075	99·65
4.	0·0076	99·86
5.	0·0100	99·86
6.	0·0100	99·72

Now, when the cresols were run in the same manner as phenol it was found that they were not completely oxidised and that they varied slightly as to the rate with which oxidation proceeded; hence, any permanganate method for their accurate determination must depend upon definitely fixed conditions.

Likewise, it was obvious that commercial creosote and guaiacol could not be determined by this procedure, since they are mixtures of several more or less related phenols that are not present in like proportion in different specimens. However, with single solutions of several common phenols and closely related compounds, fairly gratifying results were obtained. Pyrogallol, pyrocatechin, resorcinol, and hydroquinone, from all of which the CH_3 group is absent, were readily and completely oxidised.

Benzoic acid was very slightly attacked, while under similar conditions salicylic acid and salol were completely oxidised. Thus it would seem that the phenolic OH group predisposes towards a complete oxidation, and that many uninvestigated phenols and closely related compounds would give analogous reactions. In making up solutions of the several phenols, sufficient N/2 NaOH was added when necessary, to ensure ready solution. The following table is self-explanatory:—

Substance.	Percentage found.	
Pyrogallol	100·4	100·1
Pyrocatechin	100·2	99·9
Resorcinol	100·5	100·4
Hydroquinone	99·49	99·56
Salicylic acid	99·79	100·2
Salol	99·77	99·91

The alkaline permanganate method is especially applicable for the quantitative estimation of the above compounds when they occur individually in very small amounts in single solutions, or in conjunction with substances not readily oxidised.

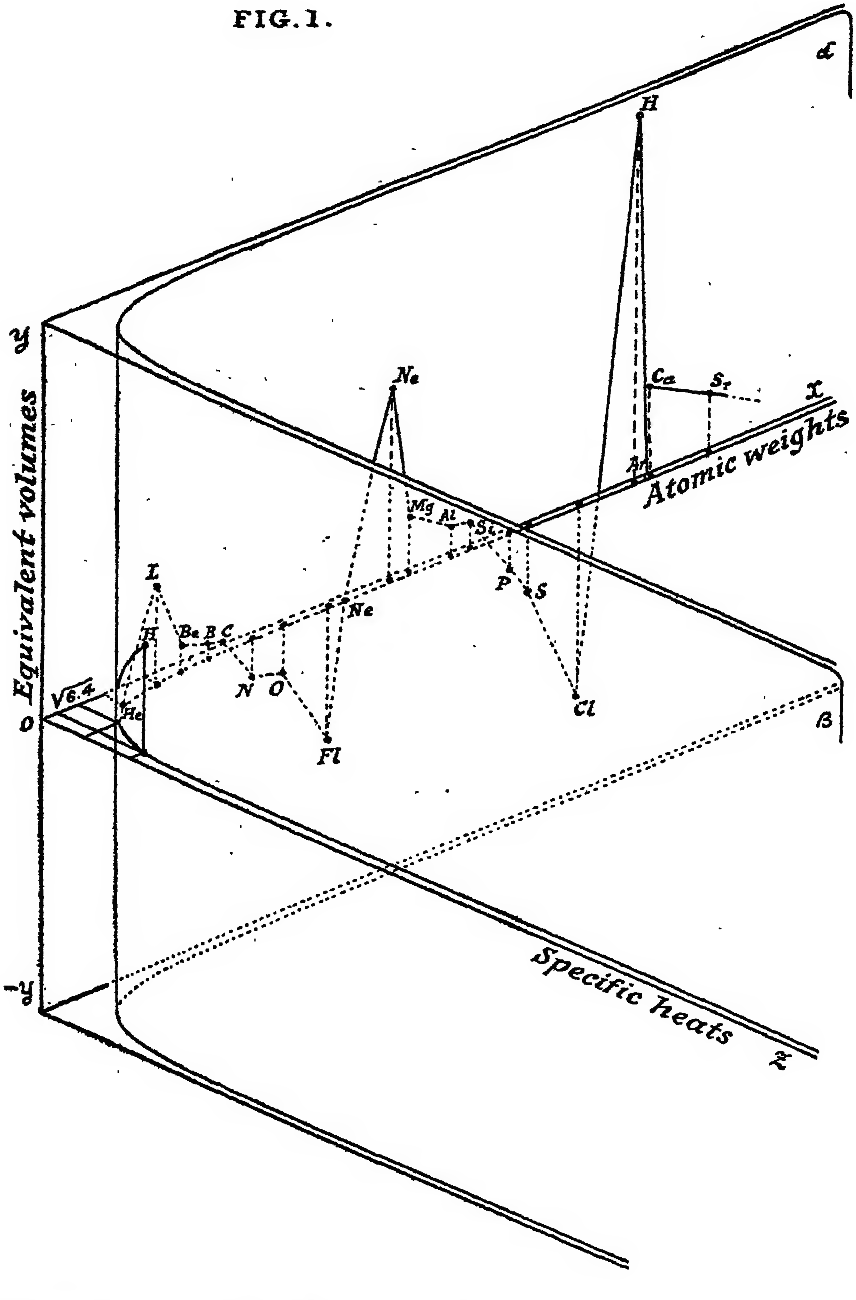
A REPRESENTATION OF THE CHEMICAL ELEMENTS BY MEANS OF POINTS IN ORDINARY SPACE.

By ARNALDO PIUTTI.

THE representation of the chemical elements on the plane of two rectangular axes, x, y, by means of points on the said plane, being based on the numerical values of two properties only, or on the quotients of these values, does not admit of extensive generalisations.

Our knowledge would undoubtedly make a notable advance in this direction if methods of representation could be used in which all the known properties of the elements which are measurable and can be expressed by numbers could be taken into consideration, but this would necessitate representing them by points in spaces of more dimensions than ordinary space, either by geometrical figures drawn on planes (if a graphic representation were required) or by means of models (if a representation in space were required), in the way in which in descriptive geometry the shapes of bodies existing in three, four, or n dimensions are represented on a plane.

FIG. 1.



Thus such methods of representation are as yet im-

possible, both owing to the fact that we have not yet obtained many numerical data referring to the properties of the elements, and moreover because these sometimes exist in many forms, so that we do not always know how to choose their constants correctly. Therefore, taking the representation of them in a plane, originally due to Borchers ("Die Beziehung zwischen den äquivalenten Volumen und Atomgewicht," Halle-a.-S., Wilhelm Knapp), and afterwards modified by C. Schmidt ("Studien über das Periodische System," *Zeit. Phys. Chem.*, 1904, lxxv., 651) by considering the elements as having positive or negative ordinates, according as they are electropositive or electronegative (whence it follows that the neutral elements are situated on the axis of x), I have limited myself to constructing a spacial representation, using, in addition to the values employed by the above-mentioned authors, the values of the specific heats of all the elements measured on a third co-ordinate axis in the following way. In working out this scheme I have availed myself of the great skill of my colleague, Prof. Del Re, and have been aided by my assistants, Magli and Perrier, to whom I owe hearty thanks.

Taking a third orthogonal axis of co-ordinates (Fig. 1) arranged in the usual way, and denoting, as in the diagrams of Borchers and Schmidt, by x the axis on which are measured the atomic weights, and by y that on which the equivalent volumes are measured, on the third axis z I have marked the specific heats of the corresponding elements, taken if possible at temperatures lying between 0° and 100° (Landolt-Börnstein, "Physikalische-chemische Tabellen," Berlin, J. Springer, 1905; "Tables Annuelles de constantes et données numeriques," vol. i., 1910;" "Recueil de constantes physiques," H. Abraham et P. Sacerdote, Gauthier-Villars, Paris, 1913).

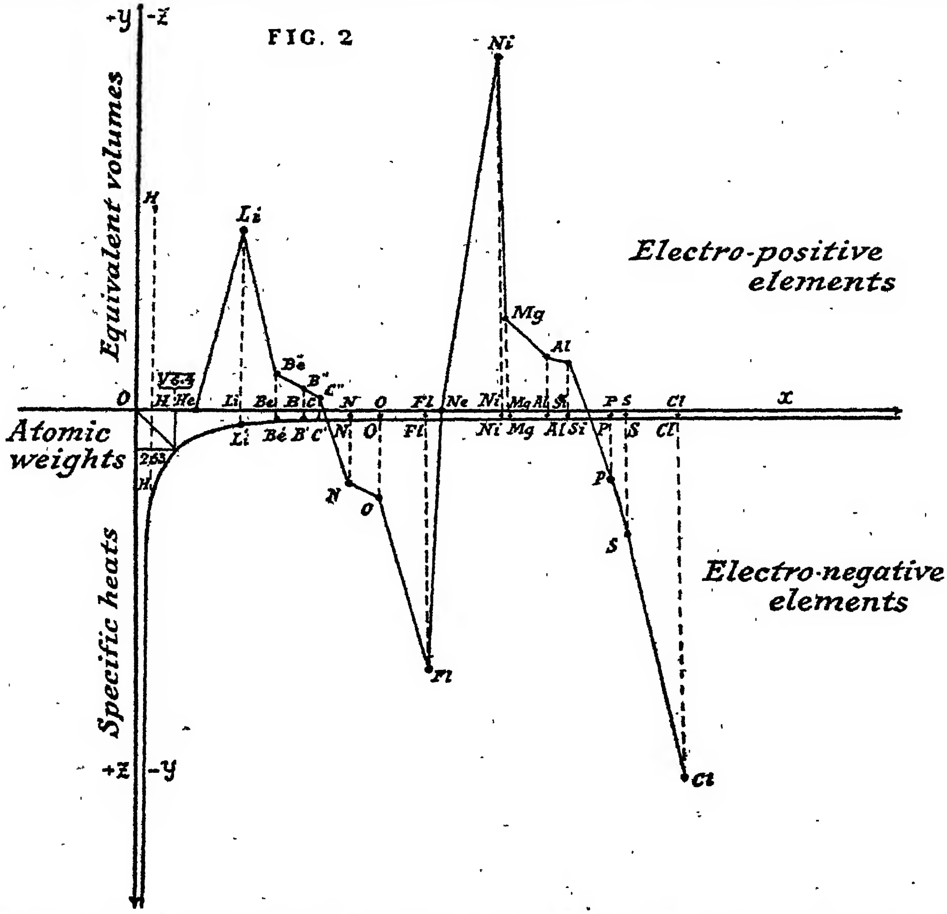
Then applying the law of Dulong and Petit, according to which the product of the atomic weight and specific heat can be regarded as nearly constant and equal to 6·4 (atomic heat), I have hence immediately deduced that on the plane xz the elements represented are projected as points the co-ordinates of which satisfy the equation $xz = 6{\cdot}4$, which is an equilateral hyperbola with the x and z axes as asymptotes.

Hence it follows that the points representing the elements *are situated on the surface of a hyperbolic equilateral cylinder*, the right section of which is the above hyperbola; in place of it we should obtian another hyperbola if we substituted another value for the constant 6·4, owing to the variation of the specific heat in dependence on the temperature. And since atomic weights and specific heats are numerically essentially positive, the said points lie on one side only of the cylinder.

If now we consider the (straight) line which is the locus of the vertices of corresponding right sections we shall find points which are on one side of the line and points which are on the other side; and those on the one side are those for which the atomic weight is greater than $\sqrt{6{\cdot}4}$, *i.e.*, 2·53 (which amounts to saying that the specific heat is less than 2·53), and those on the other are those for which the atomic weight is less than $\sqrt{6{\cdot}4}$ (and hence the specific heat is greater than $\sqrt{6{\cdot}4}$).

The line would then be the locus of the points repre-

FIG. 2



senting the elements which would have an atomic weight equal to their specific heat.

Hence arises the necessity for keeping distinct the two parts into which the line divides the surface of the cylinder of representation. For the present we will call the first semi-surface the α surface, and the second the β-surface.

Now the fact that only hydrogen is situated on the β-surface, while all the other elements yet known are arranged on the α-surface seems to me to be noteworthy; for hydrogen takes up its position thus in a spacial representation based on a property which it has in common with the other elements (atomic heat). This does not occur in the planar arrangements of Borchers and Schmidt, nor is it shown in the periodic system of Mendeleeff and L. Meyer, whilst an element which is so important and so widely distributed would be expected to take up its position among the other elements, whatever method of arrangement was chosen.

The suggestion of Mendeleeff that it should be placed at the head of the alkali metals was not confirmed by its properties in the solid state, afterwards observed by Sir J. Dewar; nor can the proposal made by him, to put it among the metalloids (*Comptes Rendus*, 1899, cxx., 451), for example at the head of the halogens, be accepted, since its properties are so different from theirs.

For this reason J. W. Retgers (*Zeit. Phys. Chem.*, 1895, xvi., 646) and L. Meyer (*Liebig's Ann.*, 1870, Suppl. vii., 357) have suggested excluding it from the periodic classification, and giving it an exceptional position, and E. J. Mills ("Numeric of the Elements," *Phil. Mag.*, 1884, [5], xviii., 393; 1886, xxi., 151) and Rudorf (*cf.*, "Das Periodische System," Leopold Voss, Hamburg and Leipzig, (1904), p. 83) have explained the fact by considering it as the last representative of a group of gases of the type of Argonian, Alnitamian, and Crucian, &c. (*Idem.*, p. 281), discovered by Sir Norman Lockyer in the fixed stars (gases of the stars λ 4451, 4457, 4649·2 respectively), and no longer existing in the solar system, or of another group called protometals (Asterium) by English astrophysicists.

And since it would be singular that one element only, viz., hydrogen, should take up its position on one semi-surface of the hyperbolic cylinder while all the others accumulated on the other, or, in other words, that elements with atomic weight less than $\sqrt{6 \cdot 4}$ would not have had, or would not still have, any other representatives, on the same semi-surface β would be found the points representing the proto elements which belong to our solar system, and from which, according to the recent theory of J. W. Nicholson (*Phil. Mag.*, 1911, xxii., 864—889), all the others are derived; for example, coronium (at. wt. 0·5131) and protofluorium (at. wt. 2·3604), to which are due some lines in the spectrum of the solar corona, and nebulium (at. wt. 1·6273) which is seen in the spectrum of the nebulæ and which, according to Nicholson's calculations, has an atomic weight lower than $\sqrt{6 \cdot 4}$, *i.e.*, 2·53, and hence must have a high specific heat like that of hydrogen.

According to this theory of Nicholson's these elements, with hydrogen, the only long-lived one on our planet, would constitute the primordial form of matter, from which all the other elements are derived, by attributing to them atomic weights deduced on a simple electron theory by equally simple combinations, particularly in the case of elements of low atomic weight. The agreement thus obtained with the experimental values is so good that we are forced to admit that it cannot be due to chance.

The grouping of the elements on the semi-surface of an equilateral hyperbolic cylinder deduced from the law of Dulong and Petit would to a certain extent confirm the views of Nicholson, besides being in harmony with the periodic system and with the arrangement given in it of the other elements, without excluding any, since those which come from radioactive transformations, according to F. Soddy (Chemical News, cvii., 97), A. S. Russell (*Idem.*, p. 49), and K. Fajans (*Le Radium*, x., 61) find their places in this classification.

Finally, to give in addition to the perspective representation which results from Fig. I. another which renders possible the direct measurement on the plane of the diagram of the constants relating to the different elements (and hence the immediate to return to the spacial determination) we may institute in the plane a system of co-ordinates of x, y, and x, z; in this system the directions of Prof. Del Re (*cf.*, "Sulle forme fondamentali dello spazio rigato, sulla dottrina degli immaginarii e sui metodi della geometria descrittiva"; L. Albano, *Accad. della Scienze*, Napoli) are followed; that is to say, a line is drawn in the plane of the diagram and an origin O is marked on it and a positive direction OX, and the perpendicular to OX is drawn through O. OX and OY, one of the lines drawn from O, are taken as the positive direction of the system x, y, and OX and the other line through O, OZ, as the positive direction of the system x, z.

In the case of any element M, as was said before, on the axis OX, starting from O, its atomic weight x is marked, and on the axis OY (in the positive or negative direction, according as the element is electropositive or electronegative) its equivalent volume y, and on the axis OZ its specific heat z, and thus two points are obtained, M′ and M″, the co-ordinates of which are x, y, and x, z respectively. These give the couple M′M″ which, as in Monge's system, represent the element M in space.

(*Note.*—In Fig. 2 the elements are marked in ascending atomic weights, ending with chlorine, for the present neglecting the position of hydrogen with regard to the other elements).

Doing this for all the elements as many points are obtained as elements are taken into consideration. They represent an arrangement the projection of which on the plane $x y$ is the configuration of Schmidt, while its projection on the plane $x z$ is the equilateral hyperbola, having for asymptotes the axis of x and the axis of z, and for semiaxis $2 \cdot 53 \times \sqrt{2}$.

As I have previously shown, our actual knowledge of the constants of the elements leads us to the conclusion that in the hyperbolic cylinder of representation only one side is utilisable; but if in cosmic conditions differing from the present elements would be able to exist with negative physical constants their representative points would evidently be found on the other surface.

I have wished to present to the Academy a preliminary notice of my attempt to represent in space the chemical elements, reserving to myself the right to develop it later as the revision of their constants or new determinations furnish me with the necessary data.—*Rendiconti della R. Accademia dei Lincei*, xxii., Series 5a, [i.], No. 9.

THE ELECTRODEPOSITION OF TIN.*

By EDWARD F. KERN.

(Concluded from p. 71.)

V. *Effect of Organic Addition-agents in Tin Electrolytes.*

There should be little difficulty in obtaining thin smooth adherent deposits of tin; but when the deposition is carried to an appreciable thickness, difficulties arise. The electrodeposits of tin have a tendency to become crystalline and brittle, more and more so the longer the electrolysis is continued (Barclay and Hainsworth, "Electroplating." 1912 Ed., p. 233).

The physical condition of electrolytically deposited metals is economically of the most importance, since the metallurgist, as well as the electroplater, wants a coherent dense smooth deposit, as the purity of the cathode metal

* Paper presented at the Twenty-third General Meeting of the American Electrochemical Society, at Atlantic City, N.J., April, 1913. From the *Chemical Engineer*, xvii., No. 6.

depends upon its density and smoothness; and, besides, the ampère-hour efficiency of a refinery is dependent upon the prevention of short circuits between anodes and cathodes. As a rule, the rougher the cathodes the lower the ampère hour efficiency and the less pure the refined metal.

The characteristic form of tin, deposited from acid electrolytes, is a mass of loose non-adherent crystals. This tendency is less apparent in neutral and in alkaline electrolytes. The concentration of the electrolyte, the temperature of the electrolyte, and the current-density, each have an effect on the character of the deposit. In general, the more concentrated the electrolyte up to saturation, and the higher its temperatures, the more coherent and smoother the deposit. Another factor influencing the deposition is one which is the result of the presence of certain organic addition-agents, which change the character of the deposit either beneficially or detrimentally.

The effect of addition-agents, when properly selected, is to cause the deposit to be smoother, denser, and more adherent. When not properly selected, the opposite effect will result—that is, the deposit will be more crystalline and less adherent, or collect as a spongy mass which drops from the cathode.

It has been found that the addition of glue or gelatin to certain tin baths, in the proportion of 1 part by weight to 1000 parts of electrolyte, has a remarkable effect on the character of the deposited tin, and, at the same time, allows the use of a higher current-density. Other addition-agents which have been found to be beneficial for certain electrolytes are glucose, saccharine, acetone, and organic salts of aluminium and iron. The effect of organic addition-agents is not permanent, so in all cases, when used, further additions must be made periodically (Barclay and Hainsworth, "Electroplating," 1912 Ed., p. 333; Fields, "Principles of Electrodeposition," 1911 Ed., p. 215).

1. Hollis's U.S. Patent 916,155 is for the use of an electrolyte containing tin fluosilicate, and to which gelatin or glue is added for the purpose of increasing the density of the deposit (*Electrochem. and Metallurgical Ind.*, 1909, vii., 224).

2. German Patent 244,567, to Matuschek, is for an electrolyte consisting of a concentrated solution of ammonium oxalate saturated with tin-ammonium chloride ($SnCl_2.2NH_4Cl$), to which an addition of black-oak tannin (quercitrinic acid) has been added. The electrolyte which he used was prepared by dissolving 200 grms. of stannous-ammonium chloride in 600 cc. of a concentrated solution of ammonium oxalate, then the addition of 50 grms. of black-oak bark tannin. This solution was electrolysed at ordinary temperature, and a solid deposit of tin was produced, when current-density of 28 ampères per sq. ft. (3 amp. per sq. dm.) was employed. The statement is made that other additions may be made to the bath, such as sodium dihydrogen phosphate, sodium silicofluoride, an inorganic acid other than nitric acid, preferably hydrofluosilicic acid, or a mixture of borax and hydrofluosilicic acid. As an example of a bath of this composition, there was added, instead of 50 grms. of tannin, to the bath given above, 6 grms. of tannin and 6 grms. of sodium dihydrogen phosphate. This bath was found to be more constant than the first.

Claims were made that much higher current-density can be employed and the electrolysis be conducted at ordinary temperature, and the deposited tin still form solid and adherent, which is not possible by using the generally employed hot alkaline electrolytes. An E.M.F. of 2 to 3 volts was maintained between electrodes 13 cm. (5½ ins.) apart, and good deposits continued to form.

The electrolyte is said to be suitable for the refining of tin, electroplating of tin, and electro-detinning of tin-plate scrap. The addition of ammonium salts, such as ammonium chloride, and organic substances, such as carbohydrates or gums, &c., is desirable for the production of brilliant deposits (*Metallurgie*, 1912, ix., 492; *Journ. Soc. Chem. Ind.*, 1912, xxxi., 440).

3. Steiner found that tin deposited from sodium sulphostannate electrolytes (see Sect. IV., 11) "could be still improved by adding a colloid to the electrolyte, for example, gelatin, as is used in the Betts process for electrolytically refining lead."

4. E. F. Kern and A. P. Frapwell conducted experiments on the effect of certain organic addition-agents on the character of electrolytically deposited tin from solutions of sodium-stannous chloride, stannous fluoride, and sodium-stannous fluoride. (Results have been previously published). These salts were selected on account of their solubility, and because their solutions are highly ionised and are excellent conductors.

(*a*) *In Sodium-stannous Chloride Electrolyte.*—The solution was prepared to contain about 80 grms. of tin and 50 grms. of sodium, as chlorides, per litre, by dissolving a calculated amount of sodium chloride in water, then adding a calculated amount of stannous chloride crystals. The electrolysis was conducted at ordinary temperature, using cast-tin anodes and tinfoil cathodes, with current-density of 10 ampères per sq. ft. (0·9 amp. per sq. dm.). The distance between electrodes was about 1¼ in. (3 cm.), and potential about 0·1 volt. The deposit formed as a mass of bright needle crystals, which soon short-circuited the electrodes.

The effect of three addition-agents — gelatin, gum-arabic, and tannin—was investigated, the electrolysis being conducted at the same temperature and current-density as above.

The presence of gum-arabic, in the proportion of 1 grm. per 800 to 1200 cc. of solution, caused the deposit to form as small bright adherent crystals, which did not short-circuit the electrodes. The electrolysis was conducted for periods of one to three hours. The gum-arabic was added as an aqueous solution. It did not cause a precipitate to form when it was added to the electrolyte.

The addition of a solution of gelatin, and of tannin, caused a white colloidal precipitate to form when added to the electrolyte. The deposit formed from electrolytes, to which the gelatin and the tannin were added in the proportion of 1 grm. per 500 to 1500 cc. of electrolyte, were a mass of small bright needle crystals which could be rubbed off with a stirring rod. These two addition-agents caused the tin to be deposited as very small needles, whereas the deposits formed in the solutions which contained no addition were long dendritic needles.

(*b*) *In Stannous Fluoride Electrolyte.*—The solution was prepared by dissolving a weighed amount of stannous chloride in a small volume of water and adding a few cc. of hydrochloric acid to clear the turbidity. The tin was then precipitated by the addition of a concentrated solution of sodium carbonate, which gave a precipitate of stannous hydroxide. This was washed free of alkali by decantation, and finally filtered. It was dissolved in moist condition in a measured quantity of 40 per cent hydrofluoric acid, to give a solution containing a very slight excess of acid. This concentrated solution was diluted, so as to contain about 80 grms. of tin per litre.

The electrolysis was conducted at ordinary temperature, using wax beakers for the cells, and cast-tin anodes and tinfoil cathodes. The current was passed at 10 ampères per sq. ft., with the electrodes about 1½ in. (3·8 cm.) apart, and E.M.F. of 0·15 to 0·16 volt. The electrolysis was carried on for periods up to eight and a-half hours.

The deposits formed, with no addition-agent present, as a mass of loosely adherent sparkling dendritic needles, which soon caused short-circuiting. The anodes were evenly corroded, and remained very bright throughout the electrolysis.

The addition-agents tried were solutions of tannin, gelatin, gum-arabic, glycerin, resorcin, saccharine, grape-sugar, and glucose. The deposits were not much altered by any of the addition-agents except tannin, gum-arabic, resorcin, and glucose. Tannin proved to be the most

effective, and resorcin and glucose less effective than either the tannin or gum-arabic. The additions were made in small amounts of the aqueous solutions at a time, the first addition being in the proportion of 1 grm. per 2000 cc. of electrolyte, then 1 grm. per 1500 cc. of electrolyte, and so on by a 500 cc. decrease in the proportion of the electrolyte, until finally 1 grm. of the addition-agent per 100 cc. of the electrolyte had been added.

In the case when tannin was used, 1 grm. per 1500 cc. of electrolyte caused the deposit to form finely crystalline and adherent. The best deposits formed when tannin was present.

The presence of gum-arabic in the proportion of 1 grm. per 1500 cc. electrolyte caused a marked improvement in the deposition. Large proportions did not prove beneficial. In no case was a dense smooth deposit formed.

With resorcin and glucose, not much improvement resulted until they had been added in the proportion of 1 grm. per 100 cc. of electrolyte, and even then the crystalline deposition was not restrained.

(c) *In Sodium-stannous Fluoride Electrolyte.*—This electrolyte was prepared in the same manner as the stannous fluoride electrolyte, with the addition of sodium fluoride. The solution contained 80 grms. of tin and 50 grms. sodium in the form of fluorides.

The electrolysis was conducted at room temperature (20° to 23° C.) in the same manner as the stannous fluoride electrolyte, but in this instance operating at current-density of 15 ampères per sq. ft. (1·4 amp. per sq. dm.). The electrodes were placed 1¼ in. (3 cm.) apart, and the E.M.F. averaged 0·18 volt. The deposit formed as bright dendritic needles, which soon short-circuited the electrodes.

The same addition-agents were used as for the stannous fluoride electrolytes, they being added at regular intervals in small amounts at a time, until an apparent change in the characteristic appearance was noticed.

Tannin in the proportion of 1 grm. per 2000 cc. of electrolyte caused the deposition of a smooth very crystalline firmly adherent coating. The run was continued for periods of six and a-half hours. The anodes corroded evenly and remained bright. The potential between electrodes varied from 0·24 to 0·26 volt. Current-density of 15 ampères per sq. ft. (1·4 amp. per sq. dm.).

Gelatin in the proportion of 1 grm. per 1000 cc. electrolyte caused the deposit to form as adherent small crystals, with a few small dendrites on the edges of the cathode. It is not so satisfactory an addition-agent as tannin.

DETERMINATION OF HYDROGEN, NITROGEN, AND METHANE IN GAS BY COMBUSTION IN A QUARTZ TUBE.*

By Prof. MATHERS and IRA E. LEE.

The purpose of this research was to devise a more convenient and a more accurate method for the determination of hydrogen, nitrogen, and methane in gas. Many different methods have been advocated for making this analysis ("Review of Progress in Gas Analysis," *Chem. Zeit.*, 1908, xxxii., pp. 801, 817). The combustion of these gases by explosion with oxygen in an explosion pipette was the method generally used until a few years ago. Results with this method in this laboratory have been very unsatisfactory. The difficulty has been that the gases were not completely burned. This gives a result for nitrogen which is too high and causes the gas to appear worse than it is.

A much better method employs the Winkler-Dennis pipette, in which the gas residue is treated with an excess of oxygen in the presence of a platinum spiral which is heated to redness by a current of electricity. This method, we think, gives accurate results when all of the conditions are favourable. The great difficulty is in fastening the spiral in such a way that no metal except platinum is exposed to the action of the hot oxygen. Base metals such as iron are readily oxidised by the oxygen. This introduces a serious error into the work. If the platinum wire for electrically connecting the coil is sealed through glass at a point near the heating coil, the glass at the joint is almost certain to crack. In most forms of the apparatus, the platinum spiral is fastened to stout iron wires which are inclosed in glass tubes. These tubes enter the pipette through holes in a rubber stopper. A cement is used to make the iron wires in the glass tubes gas tight. This form of apparatus would be satisfactory if platinum wires were used in the place of the iron wires, but this is too expensive. The ends of the iron wires in the pipette are oxidised during each combustion. This error increases the percentage of hydrogen and lowers the percentage of nitrogen. A modification of the apparatus, as devised in this laboratory, overcomes these objections and difficulties. Two short pieces of platinum wire were sealed into the ends of two glass tubes. The platinum spiral which was to be heated was fastened to two platinum wires, which were then thrust in the open ends of the glass tubes. These wires extending into the glass tubes were bent into wavy shapes, so that they would be held in position by contact with the sides of the tubes. When the pipette was filled with mercury, these glass tubes were filled (and remained filled) with the mercury, so that the electrical connection was complete from the outside platinum terminals through the platinum spiral. The places where the platinum wires were sealed in the glass were so far from the heated spiral that there was no trouble with cracking. A platinum spiral, made by twisting together several very small platinum wires, lasts much longer than a spiral made of a single platinum wire. The spiral must be smaller in diameter than any of the other pieces of platinum which are used. This apparatus gives correct results when properly manipulated.

One source of error is always present in all combustion over mercury. If the spiral is heated too hot, the mercury is oxidised, while if the temperature is so low that there is no danger of oxidising the mercury, the combustion of the gases will be incomplete. The Drehschmidt method (Hempel-Dennis, "Gas Analysis," p. 140) avoids this error, since no mercury is present during the combustion. This method of burning the gas-residue mixed with oxygen, by passing it through a hot platinum capillary tube, is perhaps the best scheme. However, the high cost of the platinum capillary tube, together with the rapid deterioration of the apparatus, makes a modification desirable. The experiments described in this paper show that the quartz tube filled with pieces of scrap platinum is an entirely satisfactory substitute for the platinum capillary tube in the Drehschmidt apparatus.

The quartz tube was 30·5 cm. long, 7·25 mm. outside, and 3·38 mm. inside diameter. Its volume, determined by the weight of mercury required to fill it, was 3·317 cc. The platinum scrap, which was used as a contact substance in the quartz tube, was prepared by cutting pieces of ordinary scrap platinum wire, which every laboratory has in quantity, into as short pieces as possible with shears. These small fragments were then placed upon stiff paper which passed through a cornet roll mill a number of times. These flattened pieces of platinum presented a large surface to the passing gas, and at the same time offered very little resistance to the passage of the gas. Two pieces of scrap platinum gauze were used, one in each end of the quartz tube, to keep the small pieces of platinum in position. The platinum weighed 11,189 grms., and had a volume of 0·522 cc. The platinum occupied 21·6 cm. of the length of the tube.

The data concerning the many preliminary experiments, which merely served to detect the errors, will be omitted.

* Paper presented at the Fifth Annual Meeting of the Indiana Gas Association, Indianapolis, Ind., March, 1913. From *Chemical Engineer*, xvii., No. 4.

The following form of apparatus and manipulation were found satisfactory:—

A mercury pipette, holding the gas to be burned and the oxygen required for the combustion, was connected to one end of the quartz tube by a suitable capillary tube with rubber connections. A mercury burette, arranged to receive the gas, was connected to the other end of the quartz tube in a similar manner. Pinch-cocks, one on the burette and one on the pipette, controlled the connections with the quartz tube. The burette was provided with a water-jacket, which was connected at its lower end with a level bottle, so arranged that the water could be drawn out and then passed back into the water-jacket. This circulation and thorough mixing of the water were necessary to prevent unequal temperatures between the top and bottom of the burette. The water-jacket was improvised from the outside part of a Liebig condenser. A thermometer, which showed the temperature of the water and gas, was suspended about midway of the burette inside of the water-jacket. The quartz tube was heated by a Bunsen burner provided with a wing tip which produced a broad flame. An asbestos board was suspended about 5 mm. above the quartz tube, to lessen the radiation of heat. The manipulation was: The temperature of the gas in the pipette—that is, the temperature at which it was measured—was carefully read. The pinch-cock connecting the burette to the quartz tube was opened and the burner was lighted for three minutes. The increase in volume of the air in the quartz tube produced by the heat was cared for in the burette. The pinch-cock connecting the pipette to the quartz tube was opened and the level bottle was raised so that the gas and oxygen passed slowly and regularly over the glowing platinum, generally about three minutes being required. In no case was there any indication of an explosion in the pipette, even when the velocity of the gas was greatly increased. The level tube on the burette was raised and the level bottle on the pipette was lowered so that the gas was forced back from the burette into the pipette. The gas was then again passed through the quartz tube over the glowing platinum into the burette. The flame and the asbestos board were removed and water was poured upon the quartz tube to cool it. After the quartz tube had reached room temperature, the pinch-cock connecting the burette and quartz was closed. The mercury in the burette and level tube was levelled. The water in the water-jacket was passed back and forth by means of the level bottle until the thermometer in the water-jacket showed constant temperature. The mercury in the burette and level tube was again carefully levelled and the volume of gas was read. The final gas volume was always corrected for variation from the initial temperature.

The process as described above was tried with pure hydrogen gas, which was prepared by the action of boiled dilute sulphuric acid upon pieces of zinc contained in a gas double pipette for solids. The pipette was filled with boiled distilled water to displace the air. The sulphuric acid was added through a glass tube which entered through the opening for the introduction of solids into the pipette. The hydrogen gas was allowed to escape completely from the apparatus several times before any was saved for analysis. This form of generator very effectively protected the hydrogen gas from the diffusion of air. The results are given in the following table:—

Hydrogen used	26·02	21·06	20·4
Air added	90·6	77·9	77·9
Volume after combustion ..	77·6	66·75	67·7
Time of experiment, minutes	2·5	2·3	3·5
Total experimental	39·03	31·6	30·6
Contraction theory	39·03	31·59	30·6

The following table shows the results which were obtained in the analysis of gas residues:—

Residue (cc.)	51·9	52·3	58·73
Oxygen (cc.)	80·4	71·3	67·18
Volume after combustion ..	50·2	42·4	38·0
Time	—	3	2
Total contraction	82·1	81·4	81·34
Carbon dioxide	18·8	17·5	17·77
Hydrogen	28·4	29·4	29·0
Nitrogen..	4·7	4·25	3·9

The result in experiment 1 was obtained with the ordinary combustion pipette. This value was taken as a standard. Experiment 2 in the table shows 17·5 per cent of carbon dioxide, which was, of course, obtained by the absorption of the carbon dioxide which was in the burette. This value must be corrected for the amount of carbon dioxide which remained in the quartz tube. The total gas residue after combustion (including the air originally in the quartz tube) was 42·4 plus 2·795 (the volume of the quartz tube which was unoccupied by platinum), which was 45·195. So, 93·8 (42·4—45·195) was the per cent of the gas which was measured in the burette. The carbon dioxide in all the gas after the combustion was 17·5—93·8, or 18·65 per cent. All carbon dioxide readings were corrected in this manner. The variations of the results in experiments 2 and 3 from the standard in experiment 1 are small and perhaps due to changes in the gas, since the three experiments were made on three successive dates. To avoid this variation from day to day, several gas residues were prepared for analysis one after noon, were mixed in a water pipette, and portions of this mixture were used for analysis. The results are:—

Residue	49·92	49·95	49·90
Oxygen	68·8	68·9	68·9
Volume after combustion	41·5	41·55	41·6
Time	2·0	3·5	3·5
Total contraction	77·22	77·3	77·2
Carbon dioxide	18·65	17·45	17·6
Hydrogen	26·6	26·65	26·5
Nitrogen	4·69	4·64	4·7
Methane	18·65	18·66	18·70

All of the results given in the tables show that the quartz tube is as accurate as the combustion pipette. It was found necessary to pass air through the quartz tube to remove the carbon dioxide produced by one experiment if another experiment were to be made at once. If only total contraction was desired, the carbon dioxide did not need to be removed. If nitrogen was to be determined, the gas remaining in the tube from previous experiment had to be removed by passing air.

This apparatus gave an excellent method of determining the total nitrogen in gas. The gas was mixed with an excess of oxygen whose nitrogen content was accurately determined. After combustion in the quartz tube, the gas was passed into potassium hydroxide to take up the carbon dioxide, and alkaline pyrogallol to take up the excess of oxygen. The unabsorbed residues consisted of the nitrogen in the gas and the nitrogen which was in the oxygen. The results are as follows:—

Gas	49·9	50·0	49·93
Oxygen	76·4	74·05	78·04
Nitrogen added in oxygen ..	7·10	6·95	7·19
Total nitrogen	8·68	8·62	8·78
Nitrogen in gas taken	1·58	1·67	1·59
Nitrogen per cent in gas ..	3·17	3·34	3·20

Other tests showed that under the conditions of the experiment less than 67·7 of the oxygen (63·4 cc. of pure oxygen) did not give complete combustion with 50 cc. of the gas. This was 12 cc. of pure oxygen in excess.

Since the work which is described in this paper was completed, Hempel, a German authority on gas analysis, has published the same method, except that he heated the quartz tube with a blast lamp. He also described an arrangement for heating a platinum spiral inside a quartz

tube with electricity. Electrical connections were made by sealing platinum wires into glass capillary tubes, which were then attached to the quartz tube by rubber tubing. Hempel says that the older methods of burning the gas were never accurate because the temperature of the platinum spiral was never high enough. He thinks that these methods which use the quartz tubes (or the platinum capillary) are the only ones which give accurate results.

After considering all of these results, one feels that the older methods of determining hydrogen, nitrogen, and methane are about to be supplanted by a new and more accurate method.

Summary.—Gas residues, after the addition of oxygen gas, were burned by passing them through a heated quartz tube which contained pieces of scrap platinum. The results are very accurate. The advantages of this apparatus over the standard combustion pipettes are :—

1. The quartz tube and pieces of platinum are not easily broken or damaged during use. The quartz tube is brittle, but will break only if struck a blow. The combustion pipette is very easily broken, and the small platinum wire often burns out, even when great care is exercised by the operator.

2. No metal or other substance which can be oxidised or acted upon by any of the gases is present in the quartz tube during the burning. In the combustion pipette, mercury, an oxidisable metal, is always present. In some of the experiments during the research, the conditions were such that very serious errors were made by the absorption of gases by the mercury. Everyone is familiar with the formation of oxides upon the mercury and upon the sides of the combustion pipette.

3. Small cracks in glass tubes, or leaks around the rubber stopper or places where glass tubes enter in the combustion pipettes, cause serious errors. There is very little chance for leaks in the quartz tube apparatus.

4. Platinum scrap, such as short lengths of wire, which we generally find plentiful in laboratories, is used in this apparatus. The quartz tubes are cheap.

5. The temperature in the quartz tube may be made high enough to insure complete combustion of the gases.

The disadvantages of this new process are :—

1. The gas becomes heated during the combustion, so care must be taken to determine the final temperature at which the gas is measured. Corrections must be made for all temperature changes.

2. A correction must be made for the carbon dioxide which remains in the quartz tube after the combustion. This disadvantage can be overcome, perhaps, by the use of a smaller bore capillary quartz tube, in which the volume is so small that a correction is unnecessary.

THE SCIENTIFIC WEEK.

(From Our Paris Correspondent).

The Speed of Hertzian Waves.

The researches made by physicists of all countries have proved that the Hertzian waves are propagated with the same speed as light, that is to say, at about 300,000 kilometres a second. Three French scholars, M. Abraham, Professor at the Conservatoire des Arts et Métiers, Major Ferrié, and M. Dufour, have, under the auspices of the Bureau of Longitudes, just determined the speed of propagation of the Hertzian waves between Paris and Toulon. Part of the results has been calculated and the speed found is 295,900 kilometres to the second, with a difference of less than 1 per cent for each determination, in comparison to the average. When all the experiments are terminated, it will be possible to have a precision of ½ per cent.

MM. Abraham, Dufour, and Ferrie propose to continue their experiments, and to study the speed of the propagation of Hertzian waves between two points separated by the sea. They intend to measure this speed between the Eiffel Tower and the Station of Wireless-Telegraphy at Washington, whilst the longitude of the capital of the United States is being determined.

Intense Cold can be Easily Obtained.

The well-known engineer, M. George Claude, has just indicated a means of obtaining the very low temperatures (so much sought after at present) by the help of liquid nitrogen that can be very easily procured in the manufactories that produce liquid air. The fact is, that by bubbling a current of hydrogen in liquid nitrogen, it is easy to obtain in vessels open to the free air the temperature of −211°, which corresponds to the solidification of the nitrogen, and thus presents the advantage of constituting a veritable fixed point.

Forest Fires.

With the first great summer heats the forest fires become so frequent that the National Society of Agriculture of Paris has considered it both prudent and urgent to seek after serious means of circumscribing them by national defences and by almost totally annihilating their effects.

M. Marchal had recently proposed to the Society counterigniferous or fire-resisting plantations, separating the forest trees by blocks or islets. M. Rivet, Professor at the Agronomic Institute, has just taken up again this excellent project and given it his support. With M. Marchal, he proposes plantations of ivy, cactus, and other fire-resisting plants of which should be formed isolating hedges.

M. Audiffred, President of the Society of Agriculture, has asked for the reports of these two specialists to be published. These reports will undergo a special study, the results of which will shortly be submitted to the consideration of the Minister of Agriculture, so as to enable the rapid establishment of a general plan for the protection of our forests against fire.

The Vegetable Riches of Morocco.

M. Pitard, Professor at the Natural History Museum of Paris, has just made a most interesting journey to Morocco. The botanical exploration of the Chaonia region has enabled him to discover the presence of 850 vegetable species, of which 657 are dicotyledons, 180 monocotyledons, 2 coniferæ, and 11 pteridophytes. This flora offers a very striking analogy with that of the Algerian Tell, and though less striking still distinctly accords with the flora of the Spanish Peninsula, which is a proof that relations relatively recent and easy existed between these two regions. At any rate, the want of numerous points in common between the flora of Chaonia and that of the Canary Isles is not a sufficiently decisive argument in favour of the non-existence of the Atlantide, for the fact is that the real canary flora being generally composed of mountainous plants, their absence in the Plains of Chaonia is natural enough, and if they exist anywhere it is on the heights of the Atlas.

Ultra-violet Action.

M. Victor Henri, Assistant in Professor Dastre's Physiological Laboratory at the Sorbonne, and M. René Wurmser have just developed a new theory concerning the action of co-ferments and of anti-ferments; by the action of ultraviolet rays on oxygenated water and on sugars, it is found that poisons paralyse the action of ultra-violet rays in the same way as they paralyse the action of ferments. The action of poisons bears, then, on the substance to be transformed, and not on the ferment as has hitherto been believed.

Radium Fixes on to the Skeleton.

M. Dominici and M. and Mdme. Laborde have injected into animals radium salts in a soluble state, and have searched the place of fixation. Fragments of bone tissue having appeared constantly radioactive during the experiments, the experimenters have tried to make a precise departure between the quantities of radium fixed by the skeleton, the muscles, the viscera, and the skin.

A rabbit was killed thirty-three days after an intravenous injection of 0·06 mgrm. of pure radium associated with an

equal quantity of bromide of radium. All the skeleton separated from the muscles, tendons, then the muscles, viscera, and skin, have all been burned separately. The ashes, weighed and analysed, showed that the radium was fixed on the skeleton rather than on the other parts of the organism, where it is found in only very feeble quantities. In their communication to the Biological Society, MM. Dominici and Laborde conclude that it is very probable that the ingestion of radium salts would have the same effect.

Considering the well-known affinity of the skeleton for salts of calcium and strontium introduced into the organism, it is quite probable that salts of radium would also go, as in the above mentioned experiments, and be fixed on the skeleton.

The Salts of Uranium Hasten certain Reactions.

In their Laboratory of Chemistry at St. Cloud, MM. Daniel Berthelot and Henri Gaudechon have just remarked that the low average produce of certain photochemical reactions, which alone has prevented their practical application outside photography, may be corrected by the employment of very small traces of uranium salts acting as catalysers.

The Conductibility of Melted Salts.

M. Tissot has recently remarked that a great number of metallic salts previously melted, then solidified and cooled, become conductors under the application of a continuous potential difference of a few volts. The phenomenon presents the following characters:—At the moment of the application of a sufficient continued potential difference the system acquires a feeble conductibility, which increases, slowly at first, then more and more rapidly. When the thickness of the lozenge of melted salt is of the order of the millimetre, the frank conductibility is established only at the end of a few minutes, fifteen to twenty, for example; but in thinner systems, that can be prepared by crushing a drop of melted salt between two platinum plates previously heated, the conductibility is more rapidly established and for a weaker potential difference. In all cases, and whatever may be the continuous potential difference applied to the system when it has become conductive, if electrical oscillations of sufficient intensity are made to act upon it, the conductibility immediately disappears. This discoheration is produced for an intensity of oscillations so much the weaker as the difference of the potential applied to the system is itself weak at the moment of the action of the oscillations. The system is, besides, apt to undergo a new coheration by the application of a suitable continuous potential difference. By leaving this difference applied during the action of the oscillation, the system can spontaneously coherate immediately the action ceases.

Although the coherers constructed up till now on this new principle are inferior as to sensibility and rapidity to those actually in use, the phenomenon is of a nature to interest physicists, for it presents a great generality. It has, indeed, been reproduced with the following salts:—Chloride of lead, chloride of thallium, bromide of cadmium, haloid salts of silver, and nitrate of silver.

Detection of Benzoic Acid in Presence of Phenols and Salicylic Acid.—Lucien Robin.—A very sensitive reaction for benzoic acid is the formation of a red amino compound when the acid is first nitrated, and the metadinitrobenzoic acid thus obtained is reduced by ammonium sulphide. A similar reaction is given by phenol, salicylic acid, &c., and hence these must be destroyed by means of potassium permanganate in sulphuric solution. The benzoic acid must be extracted by means of alcohol and sodium bicarbonate solution, the liquid must be evaporated, acidified with sulphuric acid, and heated to 80°, potassium permanganate being added drop by drop till the pink colour persists. The liquid is then allowed to cool, treated with ether, and again shaken with sodium bicarbonate solution. The benzoic acid is then detected as described above.—*Annales des Falsifications*, No. 55, 1913, p. 277.

NOTICES OF BOOKS.

A Manual of Painters' Colours, Oils, and Varnishes. By George H. Hurst, F.C.S. Fifth Edition. Revised by Noel Heaton, B.Sc., F.C.S., with a Chapter on Varnishes by M. B. Blackler, Ph.D. London: Charles Griffin and Co., Ltd. 1913.

This book has a well-deserved reputation as a text-book for the use of technical students and practical men, and the difficult task of revising another author's work has been so excellently carried out by the editor that it will undoubtedly for a long time retain its position among books upon the chemistry of paints. Every detail has undergone a careful revision, and while the original general plan has not been altered, in some cases it has been found necessary practically to re-write whole chapters. For example, the accounts of lead and zinc whites have been very greatly enlarged, and the general nature and properties of pigments are now treated more fully than before, while the chapter on varnishes has been extensively altered.

Natural Rock Asphalts and Bitumens. By Arthur Danby. London: Constable and Co., Ltd. 1913.

The author of this work has practically broken fresh ground in English literature, for no book has been published during the last twenty years upon rock asphalts, and his unbiassed account of the nature and uses of asphalts and bitumens has no rival in the language. The geology and history of the subject are treated very fully, the chapters on the latter being possibly rather overloaded with material, which, though interesting, is not of very great importance to practical or scientific men. After long accounts of the sources of asphalt in Europe and America, the extraction and preparation of rock asphalt is not reached until Chapter IX., more than half-way through the book. Here are given detailed descriptions of the practice in the mines, quarries, and factories of Eschershausen, Brunswick, followed by full and lucid accounts of modern work on methods of analysis. The author has had extensive experience of the employment of asphalt for various purposes, and states very clearly and definitely the conclusions he has come to and his reasons for them, when they differ, as they not infrequently do, from those of other authorities.

Die Anwendung Hoher Drucke bei Chemischen Vorgängen und eine Nachbildung des Entstehungsprozesses der Steinkohle. ("The Employment of High Pressures in Chemical Processes, and a Reproduction of the Method of Formation of Coal"). By Dr. Friedrich Bergius. Halle (Saale): Wilhelm Knapp. 1913. (M. 2.80).

In this monograph an account is given of the author's investigation of the effect of pressure upon chemical reactions, and the application of the results obtained to the case of the formation of coal. In many respects his work must be regarded as unfinished, and further experiments are necessary to throw light upon some points. On the other hand, from the study of the chemical and physical properties of superheated water certain definite conclusions as to the origin of coal may be drawn, and the author was well advised to publish the material he had accumulated, even although the research is by no means completed.

Physikalische Chemie der Homogenen und Heterogenen Gasreaktionen. ("Physical Chemistry of Homogeneous and Heterogeneous Gas Reactions"). By Dr. Karl Jellinek. Leipzig: S. Hirzel. 1913. (M. 30).

The object of this monumental work on the physical chemistry of gas reactions is to show what light has been thrown by modern research in physical chemistry on the nature and occurrence of gaseous reactions, and also to illustrate chemical conceptions by reference to experi-

mentally observed facts. The text is divided into four sections. The first and longest deals with the statics of gas reactions; in the theoretical part of this section the references to Planck's work are very numerous, and a thorough exposition is given of the theory of heat radiation. The experimental work which has been done on the subject is very fully described. The second section, on kinetics, is comparatively short, and deals almost entirely with homogeneous reactions, hardly any work having yet been published on heterogeneous reactions. The two last sections of the book deal with the electrochemistry and photochemistry of gas reactions, and give particularly interesting accounts of the research which has been done is the last few years in these branches of physical chemistry.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Bulletin de la Société Chimique de France.
Vol. xiii.-xiv., No. 11, 1913.

1.5.Hexenic Ether Oxides. – R. Dionneau.—Phenoxyhexene, $C_6H_5OC_6H_{11}$, can be obtained by the action of sodium on 1.3.phenoxyiodopropane, $C_6H_5O(CH_2)_3I$. On bromination it yields a dibromide, $C_6H_5OC_6H_{11}Br_2$. Excess of fuming hydriodic acid converts it into diiodohexane, $C_6H_{12}I_2$, while with the gaseous acid it gives phenoxyiodohexane, the magnesium derivative of which with water yields phenoxyhexane. Phenoxyhexene gives phenoxyvalerianic acid on oxidation.

Amino Alcohols.—M. Brenans.—The author has studied the series of amino alcohols prepared by the action of the fatty amines on the products of condensation of epichlorhydrine or dichlorhydrine with the phenols, and has also prepared some glyceric ethers of the phenols homologous with phenoxypropanediol. Aminophenoxypropanediol is specially interesting on account of its physiological action. It contains two very active groups, the amino group and the group $OCH_2.CHOH.CH_2OH$.

Fluorine in Reagents.—P. Carles.—It has been shown that fluorine is a constituent of the ashes of various vegetables, of sea-water, &c., but the author also finds that it is very difficult to obtain certain reagents quite free from fluorine. Thus nitric acid and its salts, baryta, barium acetate, sodium bicarbonate, potassium bicarbonate, ammonium carbonate, &c., always contain appreciable amounts. Hydrochloric and sulphuric acids, on the other hand, are often quite free from fluorine.

Gravimetric Method of Determining Carbonic Acid. —A. Dejeanne.—The CO_2 to be determined is precipitated by a titrated solution of baryta, strontia, or lime. Magnesium chloride solution is added, and thus a compound is obtained which is stable towards the CO_2 of the air. An aliquot part of the solution is separated, and the barium, strontium, or calcium is determined as sulphate, carbonate, or oxalate. Since the strength of the baryta solution was known the amount of CO_2 fixed can be deduced.

New Method of Determining Lactic Acid.—A. Bellet.—To determine lactic acid in complex organic substances the albuminoids are first precipitated by Patein and Dufau's reagent. The filtrate is neutralised, treated with dilute H_2SO_4, mixed with sulphate of sodium and sand, and extracted with anhydrous ether in a Soxhlet's extractor. The lactic acid is then determined as ethyl aldehyde, using the property the latter possesses of reducing an argentic ammonium-sodium solution. The author has devised a special apparatus for dropping the aldehyde into an argentic solution of known strength.

MISCELLANEOUS.

Iron and Steel Institute.—*Brussels Meeting, Sept. 1—4, 1913.*—The Autumn Meeting of the Iron and Steel Institute will be held at the Palais des Academiès, Brussels, on Monday, Tuesday, Wednesday, and Thursday, September 1st to 4th, 1913. The following is the list of Papers that are expected to be submitted:—

Armand Baar (Liége)—"Reinforced Pile Foundations for Blast-furnaces."

Prof. E. D. Campbell and F. D. Haskins (University of Michigan)—"Some Experiments of the Effect of Heat Treatment on the Colorimetric Test for Carbon in a 0·32 Carbon Steel."

Prof. A. Campion and J. M. Ferguson (Glasgow)—"A Method of Preparing Sections of Fractures of Steel for Microscopic Examination."

Baron E. Coppée (Brussels)—"The Manufacture of Coke in Belgium."

General L. Cubillo (Madrid)—"The Manufacture of Armour-piercing Projectiles."

Otto Frick (Beckenham, Kent)—"The Electric Refining of Steel in an Induction Furnace of Special Type."

Emil Gathmann (Baltimore)—"Commercial Production of Sound Steel Ingots."

Gevers-Orban (Liége)—"The Distillation of Tar in Metallurgical Practice."

E. Houbaer (Liége)—"The Use of Coke-oven and Blast-furnace Gases in Metallurgy."

Prof. H. Hubert (University of Liége)—"Present Methods of Testing, with Special Reference to the Work of the International Association for Testing Materials."

Baron E. De Laveleye (Brussels)—"A Historical Survey of the Metallurgy of Iron in Belgium."

F. Rogers (Sheffield)—"So-called 'Crystallisation Through Fatigue.'"

Prof. A. Sauveur (Cambridge University, U.S.A.)—"The Allotropic Transformations of Iron."

Dr. J. E. Stead (Middlesbrough)—"A New Method for the Determination of the Critical Points Ac_1 and Ar_1."

Dr. J. E. Stead (Middlesbrough) and Prof. H. C. H. Carpenter (Manchester)—"The Crystallising Properties of Electro-deposited Iron."

Benjamin Talbot (Middlesbrough)—"Modern Open-hearth Steel Furnaces."

Gustave Trasenster (Ougrée, Belgium)—"The Use of Oxygen in Blast-furnaces."

C. Vattier (Valparaiso)—"Note on the Principal Deposits of Iron Ore in Chili."

Members intending to take part in the discussion of any of the above papers can be supplied with copies a week before the Meeting on application to the Secretary, G. C. Lloyd, 28, Victoria Street, London, S.W.

Solubility of Active Deposit of Radium.—E. Ramstedt.—The rate of solution of the active deposit of radium depends upon the material and the surface of the body upon which it is deposited. Clean polished glass is the best to use for studying the deposit. If the induced activity is deposited on the glass as radium A only half the radium B and C formed can dissolve. On platinum and gold from 60—70 per cent dissolves. Radium C is soluble in hydrochloric, sulphuric, nitric, and acetic acids, less soluble in water, ammonia, and solutions of sodium carbonate, and very slightly soluble in organic liquids. Radium B dissolves more rapidly than radium C in water and in dilute acids, less rapidly than radium C in alkaline solutions, and only very slightly in organic liquids. The rate of solution increases with the temperature, both for radium B and radium C. Radium A is fairly soluble in the above solvents and in organic liquids. Oxygen enormously diminishes the solubility of the active deposit of radium.—*Le Radium*, x., 159.

THE CHEMICAL NEWS.

Vol. CVIII., No. 2804.

MOISTURE IN CLOTH.

By E. G. BRYANT, B.A., B.Sc.

A few weeks ago I was asked to examine some cloth that had been exposed for a short time, not more than an hour, in a shop which had been flooded with water from a fire-engine. The idea was that, during that time, it might have become so damp as to render it liable to mildew; there was no question as to its having been actually wetted. A roll of the cloth was wrapped up in waterproof paper and sent to me, together with a piece of almost identical cloth, bought in the ordinary way of business and similarly protected. Neither piece was opened in the laboratory until all preparations had been made for treating it.

The cloth was a so-called Harris tweed, though from its uniform texture and only very medium roughness and thickness, it was probably machine made. In order to test its degree of moisture I cut out six small pieces weighing from 1 to 2 grms. Three were cut near the edge and three about half-way across the breadth; one pair from the outside of the roll, one pair from about the middle, and the third pair from the innermost layers. A similar pair of samples was cut from the smaller sample which had only been exposed to the ordinary atmosphere of the locality.

Each sample was cut, weighed, and put to dry separately, the remainder of the cloth being protected meanwhile from the atmosphere; the samples were weighed between close-fitting watch-glasses. They were dried for half-an hour at a temperature not above 70° C.; further heating caused no change of weight. The percentage losses of weight were as follows:—

Sample unexposed to water	13·96
	12·78
Outside of roll	12·29
	12·8
Middle of roll	13·8
	13·09
Innermost layer	13·49
	13·25

These seemed extremely high; therefore, in order to ascertain that nothing but water had been lost, the samples were left open in the laboratory till next morning, nine or ten hours. On re-weighing them it was found in every case that the original weight had been regained within at most 5 mgs.; in one instance an actual increase of 3 mgs. was found.

Port Elizabeth is on the sea-coast, and is rather noted for a humid atmosphere. Still it is somewhat surprising to find that an ordinary piece of cloth has here a normal water content of 12 to 14 per cent. Perhaps some of your readers may be interested to compare these results with any obtained in different localities.

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Catalytic Hydrogenation of Acetylenic γ-Glycols in presence of Palladium Black.—Georges Dupont.—The mechanism of hydrogenation in presence of palladium black is different with different classes of glycols. With fatty glycols the hydrogenation of the alcoholic function acts only on the acetylenic glycol, and the saturated alcohol is not reducible. With the aromatic glycols, on the other hand, the hydrogenation is total, and from diphenyl butanediol, for example, the hydrocarbon can be obtained quantitatively.—*Comptes Rendus*, clvi., No. 21.

THE PRECIPITATION OF GOLD BY MANGANOUS SALTS.*

By A. D. BROKAW.

Some interesting occurrences of gold associated with manganese dioxide led to the suspicion that manganous salts, under certain conditions, might react with solutions of gold salts to bring about a mutual precipitation; the gold in the free state and the manganese as hydrated manganese dioxide. A search for literature on such reactions was without avail, and experiments were undertaken with a view to ascertaining if such a reaction is possible, and if so, under what conditions it can take place. The reaction in question is in a sense the reverse of the series of reactions involved in the well-known "chlorination process" of extracting gold from its ores:—

$$MnO_2+4HCl=MnCl_2+Cl_2+2H_2O$$

and

$$3Cl_2+2Au=2AuCl_3.$$

The reaction is doubtless much more complex than the summary equations, but it will be seen that a reversal of the series would lead to the formation of gold and manganese dioxide.

Auric chloride solutions of varing concentrations were mixed with solutions of manganous chloride with concentrations ranging from 0·5 N up to saturation, but no reaction was detected even when the mixture was boiled for several minutes. The addition of a very small amount of alkali to the mixtures, in the cold, caused an immediate precipitation of a dark brown mass resembling manganese dioxide in the hydrated form commonly precipitated. The precipitate was collected, carefully washed to free it from the gold solution, and then treated with standard oxalic acid, containing a small amount of sulphuric acid. The solution thus obtained was divided into equal portions; one was analysed for manganese and the other titrated for loss of oxalic acid. The results showed that for every equivalent of manganese an equivalent of oxygen had been taken up by the oxalic acid, proving the precipitate to be manganese dioxide. In a check experiment the precipitate was taken into solution with the standard oxalic-sulphuric acid mixture, which was titrated for loss of acid. The manganese in solution was then re-precipitated as hydrated manganese dioxide by a standard method, and the precipitate was again treated with the standard acid mixture. The same loss of acid as before showed the original precipitate to be manganese dioxide.

Gold was left by the solution of oxalic acid, and was readily recognised as such.

Gold chloride solutions are notably acid in their reaction, due probably to hydrolysis in part, and in part to the ionisation of an addition product with water. Hittorf and Salkowsky showed by electrolytic experiments that gold chloride solution is ionised as follows:—

$$2\overset{+}{H}+\overset{=}{AuCl_3O}.$$

Solutions of gold chloride show marked acid properties toward indicators, and apparently the acidity thus developed is sufficient to suppress the reaction

$$2Au^{+++}+3Mn^{++}=2Au+Mn^{++++}.$$

If we postulate the intermediate formation of $MnCl_4$ in minimal amounts, we are justified in assuming that the salt would be largely hydrolysed, since tetravalent manganese is a very weak base. This hydrolysis would be suppressed by the presence of acids, but on reducing the acidity hydrolysis might become effective, forming the very slightly soluble hydrated manganese dioxide, and with this removed from the equilibrium system by precipitation, the reaction might proceed until concentrations were diminished to equilibrium conditions.

It is of interest to note that the precipitation began long

* Paper presented at the Milwaukee Meeting of the American Chemical Society, March, 1913. From the *Journal of Industrial and Engineering Chemistry*, v., No. 7.

before the solutions were entirely neutralised, as shown by indicator tests. This was shown in another way by placing a crystal of Iceland spar in the mixture of gold and manganous chlorides in solution. A slight effervescence occurred, and after a few hours the crystal was covered with a brown coat of manganese dioxide in which flakes of gold were plainly visible. The precipitation of gold was practically complete when an excess of $MnCl_2$ was employed, though this solution had at least the acidity of saturated carbonic acid.

An interesting reaction of similar nature was found to take place between auric chloride solution and manganous carbonate. The precipitated carbonate (doubtless amorphous, in part, at least) reacts at once, and is turned to the dark brown hydrated dioxide. The crystallised carbonate, that is, the mineral rhodochrosite, reacts slowly, but, after a day, a crystal was coated with dark brown and flakes of gold were plainly discernible.

Summary.

If we suppose manganese tetrachloride to be an intermediate product, present only in very minute traces, we may find in it some basis of explanation. Suppose—

$$2AuCl_3+3MnCl_2 \rightleftharpoons 2Au+3MnCl_4.$$

Since tetravalent maganese is an exceedingly weak base it should be little ionised, but it may be subject to two other sorts of dissociations, namely:—

1. A molecular dissociation, $MnCl_4=MnCl_2+Cl_2$.
2. Hydrolytic dissociation,

$$MnCl_4+4H_2O = Mn(OH)_4+4HCl.$$

Theoretically we should have the hydrolysis constant

$$\frac{Mn(OH)_4 \times (HCl)_4}{MnCl_4} = K,$$

assuming hydrolysis according to the above equation. It is obvious that the presence of acid would tend to cut down the hydrolysis and allow the tetrachloride to become sufficiently concentrated to make its molecular dissociation appreciable—the greater the concentration of acid the greater this tendency—and we may, in this way, easily obtain conditions under which free chlorine is liberated, as in the chlorination process.

If, however, the acid concentration is reduced below a certain figure the concentration of the tetrahydroxide will reach saturation. Any further reduction of acidity must result in the precipitation of the hydrated dioxide. It will be seen that such an adjustment may be very delicate indeed—and this seems to be supported by the lack of success in preparing the tetrachloride, subject, as it would be, to both hydrolytic and molecular dissociation.

THE PYROSULPHATES OF SODIUM AND POTASSIUM AS CONDENSING AGENTS.

By ALLAN F. ODELL and CLEVE W. HINES.

The availability of the pyrosulphates of sodium and potassium as condensing agents seems never to have been taken advantage of except in the preparation of acrolein from glycerol, and in the preparation of certain alkyl esters of aliphatic and aromatic acids (Bogojawlenski, *Ber.*, 1905, xxxviii., 3344). The ready conversion of these salts into the bisulphates by the addition of water should be the means for their effective application as mediums to abstract water in organic syntheses.

Attention was drawn to this probability when an attempt was made in this laboratory to find a better method for the sulphonation of the mixed alkyl aryl ketones—aceto phenone in particular. This ketone could not be sulphonated satisfactorily by the use of these salts in combination with sulphuric acid. At temperatures up to that of the water-bath, acetophenone yielded triphenylbenzene in varying quantities. The greater part of the acetophenone was recovered, most of the time, unchanged. The same experiments conducted at temperatures from 140° to 200° yielded a large amount of a brittle dark coloured resin. This was probably a decomposition product of the ketone (*Ber.*, vii., 1123).

As a method for the preparation of triphenylbenzene, the experiment carried out at low temperatures is probably more convenient than the usual method of employing hydrochloric acid as a condensing agent (*loc. cit.*).

The most favourable conditions for the formation of triphenylbenzene were determined in the following experiment:—

Twenty-five grms. of acetophenone are mixed with 52 grms. of potassium pyrosulphate, freshly prepared and finely powdered, and about 4 grms. of concentrated sulphuric acid stirred into the mixture. This is then heated in a closed flask in an air-bath to 45° for thirty hours. At the end of this time the solid mass is treated once with 85 per cent alcohol to extract the unchanged acetophenone, then with hot water until the acid sulphate of potassium is dissolved. The residue remaining, when re-crystallised from glacial acetic acid, gives glistening white needles of triphenylbenzene, m. p. 172°. The yield varies from 65 per cent to 85 per cent of the theory.

This particular condensation would not take place with the pyrosulphate alone, even when heated with it in a sealed tube for six hours to 180°. Neither would it take place with sulphuric acid alone.

With the idea of testing the applicability of the pyrosulphates in other condensations, a number of experiments were carried out. The results of these go to show that these salts may be used where a mild condensing agent is required.

The general method employed consisted of mixing the substances to be condensed in the molecular proportions required and adding 1 molecule of the pyrosulphate for each molecule of water to be abstracted. In the examples given below, no solvent was used to bring about the intimate mixture of the reacting substances.

The following cases were thought to be of sufficient value to give the processes in detail:—

Benzal-aniline.—Twenty-one grms. of benzaldehyde, 20 grms. of aniline, and 52 grms. of potassium pyrosulphate are heated on the water-bath for thirty minutes. The resulting solid is treated with ether, whereby the benzal-aniline is extracted and is obtained almost pure on evaporation of the solvent. The yield is almost quantitative.

Benzal-malonic Acid.—Nine grms. of malonic acid, 10 grms. of benzaldehyde, and 28 grms. of pulverised potassium pyrosulphate are mixed and heated in the boiling water-bath for three hours. The resulting mass is treated with 150 cc. of boiling water, heating until everything dissolves, and filtered. On cooling slowly, benzalmalonic acid crystallises out in an almost pure condition, m. p. 192—195°. The yield is about 75 per cent of the theory.

Benzal-acetophenone.—Twelve grms. of acetophenone, 10 grms. of benzaldehyde, and 25 grms. of pulverised sodium pyrosulphate are mixed and heated in the boiling water-bath for six hours. The residue is treated with 75 cc. of water and boiled to dissolve the acid sulphate. The unchanged acetophenone and benzaldehyde form a layer on the top of the resulting solution, from which the benzal-acetophenone crystallises out on standing. The crystals are drained off and washed with cold water, then with dilute alcohol. The compound so obtained is almost pure, with a melting-point of 57° to 58°. The yield is about 30 per cent of the theory.

Acetanilide.—Thirty grms. of glacial acetic acid, 25 grms. of aniline, and 25 grms. of pulverised sodium pyrosulphate are heated in a flask, with an air condenser, in an oil-bath at 130—140° for one hour. The resulting mass is powdered and boiled with 300 cc. of water until everything dissolves. On cooling, acetanilide of m. p. 113° crystallises out. The yield is almost quantitative.

Efforts to produce condensation between aniline and the phenols were not so successful. Condensation apparently

took place, probably with the formation of sulphuric acid esters (*cf.*, Lassar-Cohen, *Arbeitsmethoden*, pp. 312—3, 4th Aufl.), which were combined with aniline. The products resulting from the crystallisation of the reaction mixture from water, however, consisted chiefly of aniline sulphate. These were not further examined.

When 1 molecule of benzaldehyde is mixed with 1 molecule of resorcinol and 1 molecule of potassium pyrosulphate and heated in the water-bath for twenty minutes, a presumably quantitative yield of an insoluble amorphous canary yellow product results. This contains sulphur, probably as a sulphuric ester also. The compound dissolves readily in potassium hydroxide to a deep red solution, from which it may be reprecipitated on the addition of hydrochloric acid. It does not melt below 300°. This substance will receive more thorough examination at a later date.

As condensing agents, the pyrosulphates would seem to serve excellently in instances analogous to those that have been cited. They have the advantage of being clean and convenient to handle, and do not cause the formation of resinous or tarry products when used alone. This was found to be the case in a large number of experiments which were carried out qualitatively. Furthermore, it is a simple matter to prepare them quickly by fusing the normal sulphates of sodium or potassium with slightly more than the theoretical amount of sulphuric anhydride.

Summary.

The pyrosulphates of sodium and potassium are convenient and effective as mild condensing agents.

Good results were obtained by means of these agents in the preparation of triphenylbenzene, benzal-aniline, benzalmalonic acid, benzal-acetophenone, and acetanilide.

The pyrosulphates cannot be used to condense the phenols with other substances.—*Journal of the American Chemical Society*, xxxv., No. 1.

THE BROMINE AND IODOMETRIC METHODS FOR THE VOLUMETRIC DETERMINATION OF CRESOL.

By C. M. PENCE.

OF the several methods suggested for the volumetric determination of phenol, the bromine method has received the most consideration, and in almost every instance where bromine has been used an attempt has been made to substitute iodine in its stead.

The popularity of the bromine method is no doubt due to two causes. First, to the fact that it answers the demand for a reliable method in the determination of the first member of the series, namely, phenol; second, to the ease in manipulation resulting from the use of the Koppeschaar bromine solution.

Now cresol is the next member of the homologous series; however, it presents upon treatment with bromine solution and acid problems quite different from that of phenol. Since commercial cresol is a mixture of the three isomeric phenols *o*-, *m*-, and *p*-cresol, the presence of the CH_3 group in the different positions necessitates the formation of compounds structurally unlike and empirically the same, and also causes, in the case of meta cresol, the formation of compounds both structurally and empirically different from those formed by *o*- and *p*-cresols. In 2.4.6-tribrom phenol brom, the bromine occupies both the *o* and *p*-positions. Now, in the case of *o*- and *p*-cresol the CH_3 group occupies the *o*- and *p*-positions, and only dibromcresol and dibromcresol brom compounds can be readily formed, since the CH_3 group is more difficult to replace by free Br than is a hydrogen atom. However, the CH_3 group is slowly replaced, and prolonged standing (several days) results in formation of tribromphenol brom. W. Autenrieth and F. Beuttel have recently published the results of an extensive investigation along this line ("Ueber die Bestimmung des Phenols, Salicyl Alkohols, der Salicylsäure und *p*-Oxybenzoësäure als Tribrom Phenol Brom," *Archiv. der Pharm.*, 1910, p. 112).

Meta cresol forms tribrom-*m*-cresol brom, since the CH_3 group is not in the position that the Br atom would occupy.

H. Ditz and F. Cedivoda have proposed a bromine method for cresols depending upon the difference in speed of reactions between bromine and *m*-cresol on the one hand and bromine and *o*- and *p*-cresols on the other ("Reactions of Bromine with Phenol and the Cresols, a Process for Calculating the Composition of Mixtures thereof," *Zeit. Angew. Chem.*, 1899, pp. 873 and 897; Abstr., *Analyst*, xxv., 74). If either *o*- or *p*-cresol is mixed with a known excess of bromine solution, acidified with (1 : 1) hydrochloric acid, and agitated for one minute, on adding KI and titrating with thiosulphate it will be found that each molecule of *o*- and *p*-cresols has absorbed 2 atoms of bromine. Under the same conditions each molecule of *m*-cresol will absorb 3 atoms of bromine. Now, if acidification is effected by concentrated sulphuric acid, the solution shaken for five minutes, and insoluble matter removed by filtration, 3 atoms of bromine will have combined with each molecule of *o*- and *p*-cresol, 4 atoms with each molecule of *m*-cresol.

The above method depends for its success upon definitely fixed conditions, namely, time, strength of acid, excess of bromine, &c. F. Russig and G. Fortmann have criticised this method ("Estimation of Cresol," *Zeit. Angew. Chem.*, 1901, p. 157; Abstr. *Journ. Chem. Soc.*, 1901, [2], p. 289), and H. Ditz has replied at length ("Estimation of Cresol," *Zeit. Angew. Chem.*, 1901, p. 160; Abstr. *Journ. Chem. Soc.*, 1901, [2], p. 289).

The present study of the reaction of bromine and iodine upon the different cresols was made for the purpose of finding which of the cresols were amenable to assay by processes which do not require previous knowledge concerning the percentage of product; that is, by processes dependent upon the formation of definitely fixed comparatively stable final products, namely, compounds containing 3 atoms of bromine in combination.

Samples of the individual cresols were re-distilled and volumetric solutions prepared from the distillates, small amounts of N/2 NaOH being added to facilitate solution. Aliquot portions of these solutions were used in the several determinations.

The results appearing in the tables are based upon the formation of dibromcresol brom and tribrom compounds on the one hand and diiodo compounds on the other.

Ortho cresol does not readily form a stable dibrom-*o*-cresol brom or a tribrom compound, as is evidenced in Exp. 1. However, upon one and a-half hours' standing more than sufficient Br is absorbed for the formation of these compounds, and the addition of 10 to 30 cc. of 10 per cent KI with from one and a-half to three and a-half hours' standing does not result in the liberation of the bromine necessary for the formation of either dibrom-*o*-cresol or a tribrom compound, as would occur if reaction proceeded in a manner strictly analogous to phenol (Exps. 2, 3, and 4).

Now, a greater dilution results in the absorption of a smaller quantity of bromine, but results are still too high, Exps. 5 and 6. Increased standing after addition of 20 cc. 20 per cent KI causes a reversal with practically theoretical quantities of bromine absorbed, the time of standing being materially reduced upon increase in the quantity of KI (Exps. 7, 8, 9, and 10).

An increase in concentration of bromine in contact with *o*-cresol, as is effected by larger quantities of Br solution, or a decrease in the quantity of cresol solution, results in the absorption of much more than the theoretical quantity of bromine, and even long standing in contact with increased quantities of KI, suitable reversal does not take place (Exps. 11, 12, 13, 14, and 15).

The effect due to increase in the quantity of acid is very

Ortho Cresol.

No.	Ortho cresol. Cc.	N/10 Br. Cc.	H_2O. Cc.	Conc. HCl. Cc.	Time of standing. Hrs.	Mins.	20 per cent KI. Cc.	Conc. HCl. Cc.	Time of standing. Hrs.	Mins.	Results. Per cent.
1.	20	50	175	5	0	20	10	—	1	30	94·45
2.	20	50	175	5	1	30	10	—	1	30	103·5
3.	20	50	175	5	1	30	10	—	2	30	102·7
4.	20	50	175	5	1	30	30	—	3	30	101·1
5.	20	50	275	5	1	30	20	—	2	0	100·98
6.	20	59	275	5	1	30	20 (*a*)	—	2	0	100·68
7.	20	50	275	5	1	30	20	—	14	0	99·78
8.	20	50	275	5	1	30	30	—	2	0	99·98
9.	20	50	275	5	1	30	30	—	3	30	100·17
10.	20	50	275	5	1	30	30	—	4	30	99·95
11.	20	75	275	5	1	30	20	—	2	0	109·4
12.	15	50	275	5	1	30	30	—	18	0	105·15
13.	10	50	275	5	1	30	30	—	18	0	106·85
14.	15	50	275	5	3	0	30	—	0	5	113·3
15.	15	50	275	2·5	5	0	30	—	18	0	106·9
16.	10	50	275	2·5	4	0	30	5	20	0	93·4
17.	15	50	275	2·5	5	0	30	5	40	0	86·22

No.	Ortho cresol. Cc.	N/10 I. Cc.	$CH_3COONa.3H_2O$. Grms.	Time of standing. Hrs.	Mins.	Procedure.	Result. Per cent.	Excess N/10 I. Cc.
18.	25	50	5	0	30	Diluted, added 5 cc. $CHCl_3$, titrated with N/10 thiosulphate, using starch as indicator.	93·66	± 25
19.	25	50	5	1	15		100·04	± 25
20.	25	50	5	14	0		100·71	± 25
21.	25	50	9	1	0		99·93	± 25
22.	25	50	9	2	0		100·1	± 25

(*a*) Heated to 40° C. after addition of KI.

Meta Cresol.

No.	Meta cresol. Cc.	N/10 Br Cc.	H_2O. Cc.	Conc. HCl. Cc.	Time of standing. Hrs.	Mins.	20 per cent KI. Cc.	Conc. HCl Cc.	Time of standing. Hrs.	Mins.	Result.
1.	20	50	—	5	0	1	10	—	1	0	97·9
2.	20	50	—	5	0	30	10	—	2	0	98·48
3.	20	50	—	5	1	0	10	—	1	0	99·2
4.	20	50	—	5	1	30	10	—	2	0	95·9
5.	20	50	175	5	0	30	10	—	2	0	99·6
6.	20	50	175	5	1	30	10	—	2	0	100·07
7.	20	50	175	5	3	0	10	—	18	0	99 93
8.	20	50	175	5	6	0	40	—	18	0	99·81
9.	15	50	175	5	6	0	10	—	0	5	101·11
10.	15	50	175	5	6	0	10	—	0	30	100·5
11.	15	50	175	5	6	0	10	—	1	30	100·2

No.	Meta cresol. Cc.	N/10 I. Cc.	$CH_3COONa.3H_2O$. Grms.	$NaHCO_3$. Grms.	Time of standing. Hrs.	Procedure.	Result. Per cent.
12.	25	40	9	—	1	Diluted, added about 5 cc. $CHCl_3$, and titrated with N/10 thiosulphate, using starch indicator.	118·5
13.	25	40	—	0·5	1		122·0
14.	25	40	—	2·0	1		130·0
15.	25	50	—	2·0	2		155.0
16.	25	50	9	—	2		152·0

Para Cresol.

No.	Para cresol. Cc.	N/10 Br. Cc.	H_2O. Cc.	Conc. HCl. Cc.	Time of standing. Hrs.	Mins.	20 per cent KI. Cc.	Conc. HCl. Cc.	Time of standing. Hrs.	Mins.	Result. Per cent.
1.	20	50	275	5	1	0	10	—	2	0	81·1
2.	20	50	275	5	4	30	10	—	18	0	95·73
3.	20	50	—	5	4	30	10	—	18	0	76·35
4.	15	50	275	2·5	3	0	10	—	0	5	97·34
5.	15	50	275	5	1	30	30	—	18	0	89·72
6.	10	25	200	2·5	3	0	10	—	18	0	101·8
7.	10	25	200	2·5	3	0	20	—	18	0	101·75
8.	10	25	200	5	3	0	10	—	18	0	97·7
9.	10	25	200	2·5	8	30	10	—	16	0	104·6
10.	10	25	200	2·5	4	0	30	5	20	0	84·94
11.	10	25	200	2·5	5	0	30	5	40	0	82·90

No.	Para cresol. Cc.	N/10 I. Cc.	$CH_3COONa.3H_2O$. Grms.	Time of standing. Hrs.	Procedure.	Result.	Excess. Cc.
12.	25	30	9	1	Diluted, added 5 cc. $CHCl_3$, titrated with N/10 thiosulphate using starch as indicator.	98·81	25
13.	25	30	15	1		99·56	25
14.	25	40	9	1		99·75	25
15.	25	50	9	1		99·75	25
16.	25	50	9	2		99·75	25

marked. When bromine is liberated by one-half the usual quantity of concentrated HCl sufficient reversal does not take place after addition of KI (Exps. 14 and 15). However, when an additional 5 cc. of concentrated HCl are added at the same time as the KI, the reversal causes far less than theoretical quantities of bromine to remain in combination (Exps. 16 and 17).

Thus it will be seen that practical results dependent upon the formation of a dibromcresol brom or tribrom compound cannot be obtained except by definitely fixing the several conditions of the experiment in pursuance of which a previous knowledge of the percentage of *o*-cresol is required.

Now, when iodine acts upon *o*-cresol, diiodo-*o*-cresol is formed. The reaction is reversible, and sodium acetate is added to unite with the hydriodic acid produced by the substituting iodine, thereby causing the reaction to proceed to completeness (Exps. 18, 19, 20, 21, and 22). In this case the reaction ends with the formation of diiodo compound, hence it is made the basis of the following method for the determination of *o*-cresol.

Dissolve 2 to 2·5 grms. *o*-cresol in distilled water containing about 10 cc. N/2 NaOH to facilitate solution. Dilute to 1000 cc. Withdraw 25 cc. portions and place in a 500 cc. glass stoppered receptacle. Add to the receptacle approximately 9 grms. sodium acetate, and then 50 cc. N/10 I solution. Let stand one hour, dilute with 100 to 200 cc. distilled water, added a few cc. of $CHCl_3$ to dissolve the precipitated diiodocresol, and titrate with N/10 thiosulphate, using starch as an indicator.

1 cc. N/10 I = 0·002681 grm. *o*-cresol.

Meta cresol does not rapidly form tribrom-*m*-cresol brom with the subsequent formation of tribrom-*m*-cresol upon standing in contact with KI (Exps. 1, 2, and 3). If the *m*-cresol solution stands one and a half hours in contact with the bromine and then 10 cc. 20 per cent KI are added, and solution is allowed to stand one to two hours, all the cresol is converted into tribrom *m*-cresol (Exp. 4).

Dilution permits a more rapid reaction which almost completes itself in half an hour. The addition of KI causes a complete reversal, even though the time of standing in contact with free bromine has been much prolonged (Exps. 5, 6, 7, 8, 9, 10, and 11).

It is thus apparent that *m* cresol may be determined by a conversion into the tribrom compound.

Upon the other hand, when iodine acts upon *m*-cresol in the presence of sodium acetate or sodium bicarbonate, a diiodo compound that may be made the basis of calculation is not produced (E. Richard, "Preparation of Iodo Derivatives of Phenol," *Journ. Pharm. Chem.*, 1902, xv., [5], 217; Abstr. *Journ. Soc. Chem. Ind.*, 1902 p. 423; Messenger and Vortmann, "New Class of Iodated Phenols," *Ber.*, xxii., 2312; Abstr. *Journ. Chem. Soc.*, 1889, p. 1150). More than the theoretical quantity of iodine is absorbed (Exps. 12, 13, 14, 15, and 16).

Para cresol absorbs bromine much more slowly than either of the other cresols. Under similar experimental conditions, four and a-half hours' standing in contact with free bromine results in absorption of only 95·73 per cent of the theoretical quantity (Exps. 1, 2, and 3). If concentration of free bromine is increased and the usual quantity of HCl decreased one-half, the bromine in combination exceeds the amount necessary for the formation of a dibrom-*p*-cresol brom or tribromcresol compound, and eighteen hours' standing does not result in sufficient decomposition even though the quantity of KI is doubled (Exps. 4, 5, 6, 7, 8, and 9).

However, an increase in both HCl and KI results in a most pronounced reversal ("Zur Quantitativen Bestimmung des Phenols auf Parakresols in Gemischen derselben und ihre Anwendung and den Harn," *Pharm. Zentralhalle*, 1911, p. 1288), which is due to the decomposition of dibrom-*p*-cresol brom into dibrom-*p*-cresol (Exps. 10 and 11).

Here, again, the result is directly dependent upon conditions, and previous knowledge is necessary on the part of the operator.

Now, when iodine reacts with *p*-cresol in presence of the condensing agent sodium acetate, diiodo-*p* cresol is formed in theoretical quantity if sufficient time is allowed for reaction to complete itself.

This reaction is made the basis of a method for the determination of *p*-cresol (Exps. 12, 13, 14, 15, and 16). The procedure is exactly the same as that given under *o*-cresol.

Summary.

1. Usual bromine methods for determination of cresol depend upon fixed conditions presupposing a previous knowledge on the part of the operator, and while they may be of service they do not satisfy the demand for a desirable method.

2. Tribrom-*o*- and *p*-cresol brom compounds cannot be formed in a manner analogous to the production of 2.4.6-tribrom phenol brom. Dibromcresol brom compounds are formed, and finally tribromphenol brom; however, *o*- and *p*-cresols cannot be determined volumetrically by a conversion into these compounds.

3. Meta cresol is determined by a conversion into tribrom-*m*-cresol.

4. Ortho and para cresols form diiodo compounds, and this reaction is made the basis of a method for their determination.

5. Meta cresol does not yield diiodo compounds under the same conditions; hence, cresol U.S.P. or any mixture containing *m*-cresol cannot be determined by a volumetric iodine method.—*Journal of Industrial and Engineering Chemistry*, iv., No. 7.

REACTIONS OF OZONE WITH CERTAIN INORGANIC SALTS.*

By YOSHITO YAMAUCHI.

Several workers, among whom we may mention Schönbein, Williamson, Maquenne, and Mailfert, have studied the oxidation of certain inorganic salts by ozone, but report, for the most part, only the final products of the reactions and not the way in which the ozone has acted to bring them into existence. The author has therefore, at the suggestion of Prof. M. Chikashige, sought to get more accurate information upon this point, and presents the following as a brief account of his investigation:—

I. *Method of Investigation.*

Estimation of the Ozone which is to be used for Oxidation.—To determine the concentration of ozonised oxygen before consuming it, there has existed only one method, that of directly weighing a certain known volume of it and of comparing this weight with that of an equal amount of pure oxygen. Since this method is by no means convenient, the author contrived a new one, that of filling two large cylindrical glass tubes of known volumes with one and the same sample of ozone, so that he could use one for the purpose of estimation and the other for the oxidation.

Take two tubes, A and B, of nearly equal capacity, 35 cm. in length, and about 5 cm. in diameter. They are provided with glass cocks, *a* and *a'*, at one end, and with double cocks, *b* and *c* and *b'* and *c'*, at the other. They are mounted in a somewhat slanting position, and connected with a bent tube at the lower end. Fig. 1 represents the arrangement. Keeping now all the cocks open, ozonised oxygen is passed first from A to B, then from B to A, the amount of the gas passed each time being almost 1·5 times more than the total volume of the two tubes. Working regularly in this manner it was always found that the amount of ozone in both tubes stood almost in a constant ratio, as will be seen below.

* *American Chemical Journal*, xlix., No. 1.

Comparison of the Amount of Ozone in the Two Tubes.—After having filled the tubes with ozonised oxygen, close all the cocks except *c* and *c'*, and disconnect the tubes. Take then two aliquot portions of a neutral potassium iodide solution, and pour them each into two different beakers, from which transfer them separately into the spaces between *b* and *c*, and *b'* and *c'*, respectively. Then, shutting off the cocks *c* and *c'* and opening the others, *b* and *b'*, let the solutions into the cylindrical parts of the tubes, and shake vigorously until they no longer give the odour of ozone. The solutions now containing liberated iodine are thoroughly washed down into their original vessels, and, after being acidified with a few drops of dilute sulphuric acid, are titrated for iodine by means of a standard solution of sodium thiosulphate (*cf.* Treadwell and Anneler, *Zeit. Anorg. Chem.*, 1906, xlviii., 87). The amounts of the ozone corresponding to these quantities are calculated from the well established equation:—

$$O_3+2KI=K_2O+O_2+I_2 \quad . \quad . \quad . \quad . \quad 1.$$

The amount of ozone thus found in the two tubes is compared after being re-calculated on the basis of a litre volume and the mean ratio taken from six such determinations, as will be seen in Table I.

Now, by the aid of this, we can easily calculate the amount of ozone in one tube, upon actually finding that in the other.

Manner of Ozone Decomposition during the Process of Oxidation.—Taking a known amount of ozone, the author caused it to act upon a salt in solution, whose amount was known and was greater than one equivalent as compared with the ozone used. When the reaction was over, he estimated the amount of the oxidised salt, from which, by taking account of the amount of ozone used, he could directly infer how the oxone decomposed before the oxidation; whether as—

$$O_3=O_2+O \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 2,$$

where only one-third the oxygen atoms would have entered into the reactions, or as—

$$O_3=3O \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 3,$$

where all three atoms would have taken part in the oxidation. With the aid of such inferences, he established chemical equations to represent the oxidising action of ozone according to the various cases.

Table I.

No.	Ozone in grm. Per 671 cc. (Tube A).	Per litre (*a*).	Ozone in grm. Per 693 cc. (Tube B).	Per litre (*b*).	*a*/*b*.
1 ..	0·0058	0·0087	0·0062	0·0089	0·98
2 ..	0·0053	0·0080	0·0058	0·0083	0·96
3 ..	0·0048	0·0071	0·0044	0·0064	1·11
4 ..	0·0081	0·0120	0·0087	0·0126	0·95
5 ..	0·0032	0·0048	0·0032	0·0046	1·04
6 ..	0·0147	0·0219	0·0151	0·0217	1·01
			Mean ..	.. ..	1·01

II. *Reactions of Ozone Investigated according to this Method.*

1. *Arseniaus Acid.*—That metallic arsenic is oxidised by ozone finally to arsenic acid was first made known by Schönbein (*Liebig's Ann. Chem.*, 1854, lxxxix., 288). The determination of ozone by the use of arsenious acid is based on this reaction (Thénard, *Comptes Rendus*, lxxv., 174; Hartley, *Journ. Chem. Soc.*, 1881, xxxix., 120; Treadwell and Anneler, *Zeit. Anorg. Chem.*, 1906, xlviii., 94).

The author took a known amount of ozone contained in a cylindrical tube, let in an aliquot portion of a neutral potassium arsenite solution, and allowed the mixture to react for about half-an hour, the quantity of the oxidised salt being then calculated from the amount of the unchanged arsenite, as determined by the use of a standard iodine solution. The ratio of the ozone to the arsenite oxidised is given in Table II.

Table II.

No.	Ozone, in grm.	Arsenious acid oxidised by the ozone, in grm.	Arsenious acid per grm ozone, in grms.
1 ..	0·0093	0·0204	2·19
2 ..	0·0080	0·0149	1·86
3 ..	0·0059	0·0138	2·34
4 ..	0·0116	0·0243	2·10
5 ..	0·0098	0·0215	2·19
		Mean	1 : 2·14

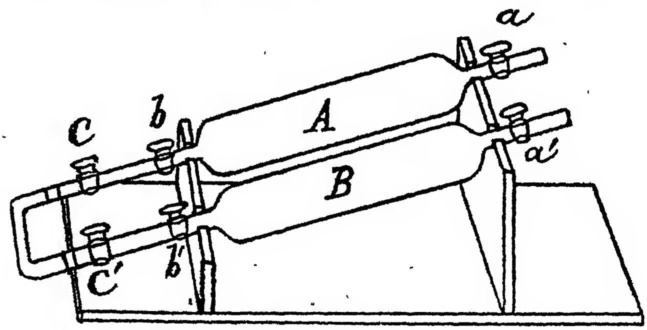


Fig. 1.

This reaction is therefore well represented by the usual equation—

$$As_2O_3+2O_3=As_2O_5+2O_2 \quad . \quad . \quad . \quad . \quad 4,$$

as it requires 2·06 grms. arsenious oxide per grm. ozone.

2. *Stannous Chloride.*—The conversion of a stannous into a stannic salt by ozone has been studied by Schönbein (*Liebig's Ann. Chem.*, 1854, lxxxix., 293) and Williamson (*Ibid.*, 1847, lxi., 14). If the reaction is, as in other cases,—

$$3SnCl_2+6HCl+3O_3=3SnCl_4+3H_2O+3O_2 \quad . \quad 5,$$

the amount of the stannous chloride oxidised by ozone would be in the ratio of 3·96 grms. to 1 grm. of the latter. But if the reaction takes place as follows:—

$$3SnCl_2+6HCl+O_3=3SnCl_4+3H_2O \quad . \quad . \quad 6,$$

the ratio would be 11·87 grms. stannous chloride to 1 grm. ozone; besides, the pressure in the reaction tube would be then very much reduced, since oxygen is no longer produced in a volume equal to the ozone consumed.

According to the author's experiments the reaction seems to proceed exactly as shown in Equation 6, and not as in 5. After a known quantity of a stannous chloride solution in hydrochloric acid had been mixed in the usual manner with a known quantity of ozone, and left for about half-an-hour with constant shaking, the amount of the stannous chloride entering into reaction was calculated from the amount of the unoxidised salt, which was found

by the use of a standard iodine solution, subtracted from the total amount of the salt taken. The results of the experiments are given in Table III.

TABLE III.

No.	Ozone, in grm.	Stannous chloride oxidised by the ozone, in grm.	Stannous chloride per grm. ozone, in grms.
1 ..	0·0077	0·1147	14·89
2 ..	0·0119	0·1550	13·03
3 ..	0·0089	0·1392	15·64
		Mean	1 : 14·52

This ratio nearly coincides with that calculated from Equation 6. That it is a little more than the latter is due, perhaps, to the simultaneous action of the co-existing ordinary oxygen. It must, however, not be forgotten that what causes the reaction for the main part is the ozone and not the oxygen, because the reaction goes on very rapidly only at first, and as soon as the ozone is used up, the reaction becomes notably slower. Thus the two tubes, A and B, were equally filled with ozone, and treated with equal quantities of a stannous chloride solution. One of the tubes was then left for only twenty minutes, and the other for a much longer interval of time. The oxidation stopped after a certain lapse of time; the degrees of oxidation in both tubes, expressed in terms of the stannous chloride, were nearly the same in spite of so great a difference in time. The results of four such experiments are given in Table IV.

TABLE IV.

Time, in minutes.	Degrees of oxidation in terms of stannous chloride.	r/t.
20	0·1368	1/1·07
140	0·1468	
20	0·2015	1/1·05
100	0·2120	
20	0·1795	1/1·15
60	0·2062	
20	0·2255	1/0·95
40	0·2133	
	Mean	1 : 1·06

Hence, we have here a new instance of oxidation by ozone, in which the latter acts by decomposing itself according to Equation 3.

3. *Sodium Thiosulphate.*—The action of ozone on sodium thiosulphate seems not to have been studied hitherto by any chemist. When a solution of this salt is shaken with ozone, it becomes milky through the separation of sulphur, while the solution, which remains quite neutral during the reaction, contains sulphite and sulphate, besides some unchanged thiosulphate.

Whether or not a part of the sulphite and sulphate comes from the oxidation of the precipitated sulphur by ozone cannot yet be definitely decided, because sulphur is oxidisable, according to Mailfert (*Comptes Rendus*, 1882, xciv., 1186), while according to Schönbein (*Liebig's Ann. Chem.*, 1854, lxxxix., 282) it is not. With regard to the author's experiment, in which he passed ozone a long time through the precipitated sulphur with neutral reaction suspended in water, he could find only an almost insignificant quantity of sulphite formed. However, in order to make the problem as simple as possible he did not take into account the presence of sulphite from such a source.

Then the quantitative estimation of the reactions was effected in the following manner:—

As usual, a known amount of a sodium thiosulphate solution was introduced into the tube containing a known amount of ozone, and the mixture was allowed to stand for about half-an-hour with frequent shaking. After being separated from the precipitated sulphur, the solution was then examined for its iodine equivalent (6, V.); the latter covers the amount of both the thiosulphate in excess and sulphite. Barium chloride was added to this solution, precipitating all the sulphates, a part of which had been originally present through the oxidation of the thiosulphate by ozone, and the rest derived from the sulphite oxidised by iodine. The amount of the sulphates (1, V.) therefore corresponded to the total weight of the thiosulphate entering into reaction (2, V.) with a definite volume of ozone (*cf.*, Equation 9). Then from the excess (4, V.) of the thiosulphate originally taken (3, V.) over that actually entering into reaction (2, V.), may be directly calculated its iodine equivalent (5, V.), and the difference (7, V.) between this value and that determined before (6, V.), which is a little greater, gives exactly the amount of the sulphite, the amount of the thiosulphate corresponding to it being then calculated from it (8, V.). The amount of the thiosulphate changing into the sulphate (9, V.) can be also calculated by taking the difference of the above quantity from the total amount of the thiosulphate entering into the reaction (2, V.). The ratio of the thiosulphate changing either into the sulphite or into the sulphate becomes nearly 1 : 2 from the mean of four such experiments, as will be seen from Table V.

TABLE V.

No.	Description.	I.	II.	III.	IV.
1.	Barium sulphate found	0·0733	0·1244	0·0826	0·1024
2.	Sodium thiosulphate entering into reaction (calc. from 1)	0·0496	0·0843	0·0560	0·0694
3.	Sodium thiosulphate originally taken (found)	0·1606	0·1606	0·1606	0·1606
4.	Excess of sodium thiosulphate escaping the reaction (diff. between 3 and 2)	0·1110	0·0763	0·1046	0·0912
5.	Iodine equivalent to the above salt (calc.) . ..	0·0891	0·0613	0·0840	0·0732
6.	Iodine equivalent to the thiosulphate solution soon after the reaction with ozone (found) ..	0·1146	0·1142	0·1144	0·1148
7.	Difference between 5 and 6	0·0255	0·0529	0·0304	0·0416
8.	Sodium thiosulphate changing into the sulphite (*a*) (calc. from 7)	0·0159	0·0329	0·0190	0·0259
9.	Sodium thiosulphate changing into the sulphate (diff. between 2 and 8)	0·0337	0·0514	0·0370	0·0435
10.	Ratio of 8 to 9	1 : 2·1	1 : 1·6	1 : 2·0	1 : 1·7
	Mean, 1 : 2.				

(*a*) From the equation $2I + Na_2SO_3 + H_2O = 2HI + Na_2SO_4$ we see that two atoms of iodine are equivalent to to 1 molecule of sodium sulphite, which is now in its turn equivalent to 1 molecule of sodium thiosulphate.

Hence we find that 2 molecules of sodium sulphate are always produced together with 1 molecule sodium sulphite. Perhaps we have no other way of understanding this reaction than by supposing it to take place in two successive stages. The first is the catalytic decomposition of the thiosulphate into sulphite and sulphur, where the ozone effects no oxidation at all; thus—

$$3Na_2S_2O_3 = 3Na_2SO_3 + 3S \quad . \ . \ . \ . \ 7.$$

Then follows the second stage, in which only two out of the 3 molecules of sodium sulphite are acted upon by ozone, so that the reaction may be expressed as follows:—

$$2Na_2SO_3 + 2O_3 = 2Na_2SO_4 + 2O_2 \quad . \ . \ . \ 8.$$

Since we know the amount of ozone necessary to effect the oxidation of thiosulphate, as shown in (9, V.), into

sulphate, we can calculate the amount of the oxidised thiosulphate per grm. ozone, thus :—

Table VI.

No.	Ozone, in grm.	Sodium thiosulphate changed into the sulphate, in grm.	Sodium thiosulphate per grm. ozone. in grms.
1 ..	0·0101	0·0337	3·34
2 ..	0·0173	0·0514	2·97
3 ..	0·0111	0·0370	3·33
4 ..	0·0139	0·0435	3·13
		Mean	1 : 3·19

Calculated for 1 molecule sodium thiosulphate per molecules ozone, as may be deduced from Equation 8, we have the ratio 1 : 3·29, which is really in good accord with the experimental ratio.

Combining now the two Equations 7 and 8, we establish the following to account approximately for the whole course of the reaction of ozone with sodium thiosulphate :—

$$3Na_2S_2O_3+2O_3=2Na_2SO_4+Na_2SO_3+2O_2+3S \quad . \quad 9.$$

(To be continued).

IMPROVING THE QUALITY OF ALUMINIUM.

Aluminium is a very useful metal, although it is so comparatively new to us ; but like other metals it has its faults, which we seek to neutralise by alloying it with other materials, since the action of heat upon it does not effect any desirable changes therein, as is the case with steel.

Among the experiments that have been made in the way of alloying are those with cobalt, the results of which have not become very generally known, and which are especially interesting when the action of this alloy is increased by the addition of tungsten and molybdenum.

Scientific researches into the chemical relation of aluminium and cobalt in alloy form go to show that those two metals are so to say soluble in each other. Of the various alloys that have been made and studied, the one with the least percentage of cobalt had one-third of this metal therein ; its solidifying point being somewhat above 100° C. Between this compound and aluminium there is a "eutectic" containing only 0·5 per cent of cobalt and having a melting-point lower than that of pure aluminium. There is also in the curve showing the melting-points of the aluminium-cobalt alloys a decided kink at the point corresponding to 20 per cent of cobalt.

With 9 to 12 per cent of cobalt there are obtained alloys that are almost free from bubbles, although the fracture is somewhat coarse and crystalline ; and although the tensile strength is not much above that of pure aluminium the alloy is more readily turned and polished, &c., and much more resistant to atmospheric influences. These alloys are still quite light and much more workable than pure aluminium. The lack of tensile strength is due to the coarse crystalline fracture, but this may be improved by the addition of tungsten (which the Germans call "wolfram") and molybdenum, so that by the help of these an alloy with but a small percentage of cobalt has three times the tensile strength of aluminium, and is also malleable and ductile. These alloys run about 0·8 to 1·2 per cent tungsten, 8 to 10 per cent cobalt, the rest aluminium.

The more cobalt these alloys contain, the less readily can they be rolled, but the greater their tensile strength ; so that those with high cobalt percentage are better for castings, the poorer ones better for forging and rolling. The alloys of molybdenum, cobalt, and aluminium run from 0·6 to 1 per cent molybdenum, 9 to 10 per cent cobalt, the rest aluminium ; these follow about the same general rules as those of wolfram, cobalt, and aluminium, except in the matter of hardness, in which they are inferior to the corresponding tungsten-cobalt alloys.—*Chemical Engineer*, xviii., No. 5. (From *Metal Industry*.)

ANALYSIS OF MILK AND MILK PRODUCTS.*

The methods employed for the analysis of milk and milk products are, in the main, those published and recommended by the United States Department of Agriculture. In the case of some of the determinations, however, it has been found that the desired information may be obtained through simpler and more rapid procedures than those of the official methods.

The following determinations are regularly made :— Total solids, ash, fat, casein, lactose, and number of bacteria per cubic centimetre.

The Determination of Total Solids.—A sample of about 5 grms. is weighed into a flat aluminium dish and evaporated to constant weight in a water-jacketed air-bath heated to boiling temperature. The final weighing must be made very rapidly to avoid absorption of water from the air.

Ash.—About 20 grms. of samples are weighed into a tared platinum dish, 6 cc. of nitric acid (sp. gr. 1·42) added, and the whole evaporated to dryness on the water-bath. The residue is finally ignited at the lowest possible temperature in an electrically heated muffle until the carbon is completely burned out, leaving a white ash. The whole is then cooled in a desiccator and weighed.

Total Nitrogenous Matter.—A combination of the official Kjeldahl and Gunning methods is used, for which the following reagents are required :—

1. An accurately standardised solution of hydrochloric acid, of about tenth normal strength. This should be standardised by precipitation of the chlorine as silver chloride, which is weighed in a Gooch crucible.

2. A standard alkali solution (NaOH) whose value in terms of the above acid is accurately known. It is convenient to have these solutions exactly equivalent to each other.

In all titrations cochineal is recommended as an indicator. It is prepared as follows :—3 grms. pulverised cochineal is extracted for several days, with frequent shakings, with a mixture of 50 cc. alcohol and 200 cc. distilled water, and the whole filtered.

Pure sulphuric acid, sp. gr. 1·84, a saturated solution of NaOH, a solution of potassium sulphide, 40 grms. per litre, powdered potassium sulphate, pure mercury, and some small lumps of pumice stone are also required.

Upon these reagents blank determinations should be made to make sure that all are nitrogen free, or to provide a constant correction.

Procedure.—A 5 grm. sample of milk is placed in the Kjeldahl digestion flask (used also for the distillation), where it is mixed with 10 grms. K_2SO_4 and 0·66 grm. of mercury, and 25 cc. of conc. H_2SO_4 added. The mixture is heated gently until frothing ceases, and then digested at the full heat of the naked Bunsen flame until colourless or nearly so, and a short time after that point is reached. This should require less than two hours, a much shorter time than either of the official methods.

When the digestion is complete, the flask and contents are allowed to cool, and the solution diluted to 200 cc., a few pieces of pumice being added to prevent bumping and 25 cc. of K_2S solution to precipitate the mercury. The acid is then neutralised and the ammonia liberated by the addition of 60 cc. of the strong alkali solution, the solution being poured down the side of the inclined flask so that it may not mix with the acid solution. The flask is connected with the block tin condenser by means of a bulb tube to prevent any of the alkali solution from being carried over mechanically, and the end of the delivery tube of the condenser placed under the surface of 40 cc. of the N/10 acid in an Erlenmeyer flask. When all is ready, the distillation flask is rotated to mix the solutions, and heat applied. The whole is boiled briskly until about 150 cc. of distillate has passed over, this being sufficient to

* Method of analysis used in the laboratories of the Armour Institute of Technology. From the *Chemical Engineer*, xviii., No. 1.

assure the elimination of all ammonia. At this point the delivery tube is disconnected, the flask removed, and its contents titrated with the standard alkali. The net volume of acid solution times the factor gives net volume of N/10 acid which is equal to vol. of N/10 NH_3 and of N/10 nitrogen which has a strength of 1 cc. = 0·0014 grm.,

so $\frac{\text{cc. N/10 acid used} \times 0\cdot0014}{\text{Wt. sample}} \times 100 = \text{per cent N.}$

Per cent nitrogen × 6·38 = per cent nitrogenous compounds.

It is frequently desirable to determine pure casein as well as total nitrogenous substances. Casein may be determined in the following way:—

1. A sample of 10 grms. of the fresh milk is made up to 100 cc. with water at 40° to 42° C. in a beaker. To this is added at once 1·5 cc. of a 10 per cent solution of acetic acid. The solution is stirred and allowed to stand for from three to five minutes, when it is decanted through a filter, the precipitate washed several times by decantation, using cold water, and finally transferred to the filter and the washing completed. The precipitated casein may run through the filter at first. In this case, the filtrate should be returned to the filter until it is perfectly clear. The precipitate obtained is run for nitrogen by the method described for total nitrogen.

Per cent nitrogen × 6·38 = per cent casein.

The difference between the total nitrogenous material and the casein is approximely equal to the albumen.

Fat.—For this determination two methods are given:—

1. The Babcock method.
2. A gravimetric method.

1. The Babcock fat test requires a special apparatus, consisting of a centrifuge capable of about 1000 revolutions per minute, and properly graduated bottles and pipettes.

A sample of 17·6 cc. of the thoroughly mixed sample of milk is pipetted into the test bottle and 17·6 cc. of commercial H_2SO_4 (sp. gr. 1·82—1·83) added. After mixing the solution is whirled in the centrifuge for four minutes. Hot water is added up to the neck of the bottle and the bottle whirled for one minute, and finally boiling water again added until the layer of fat comes within the scale, and the whole again whirled for one minute. The readings on the scale give per cent of fat direct.

2. The gravimetric method for fat is carried out as follows:—

A paper coil is prepared by rolling strips of thick filter paper, 2·5 by 25 inches, into solid rolls. Such paper coils may also be purchased prepared for use. They should be thoroughly extracted with ether before use.

About 6-8 grms. of milk is weighed in a weighing bottle, and about 5 cc. of this absorbed into the paper coil, care being taken to keep one end of the same dry. A second weighing of the bottle and the milk remaining gives the weight of the sample, which should be about 5 grms. The sample is dried thoroughly in a water-jacketed air-bath, and is then extracted in a Soxhlet or similar type of extraction apparatus for several hours with petroleum ether. After 6 hours the ether is evaporated off and the fat weighed.

Lactose.—The determination of lactose or milk sugar is most conveniently made by means of the polariscope, such as is used in sugar analysis, and which reads percentage of cane-sugar direct. Lacking such an instrument, the gravimetric method is satisfactory, though somewhat longer.

1. *Optical Method.*—For this a sugar polariscope or saccharimeter is employed, whose normal weight for sucrose is 26·048 grms.

By using a constant, exact weight of sample based upon the specific rotary power of pure lactose, it is possible to make the polariscope read percentage direct.

To get the exact weight, it is best to determine the specific gravity of the milk, either by the Westphal balance or by a delicate hydrometer, and then measuring accurately the volume corresponding to the sp. gr. in the appended table:—

Table for instrument whose normal weight for sucrose is 26·048 grms.:—

Sp. gr.	Volume of milk, cc.
1·024	64·30
1·026	64·40
1·028	64·15
1·030	64·00
1·032	63·90
1·034	63·8
1·035	63·7

The volume indicated from the table is run into the flask that corresponds to the instrument in its graduation, and to it is added 30 cc. of a mercuric iodide solution (33·2 grm. KI, 13·5 grms. $HgCl_2$, and 20 cc. glacial acetic acid dissolved in 640 cc. of water), the whole made up to the mark of the flask and mixed thoroughly. It is then filtered through a dry filter, a portion put into the polariscope tube and the readings made.

100 mm. tube reads per cent direct.
200 mm. tube reading is divided by 2.
400 mm. tube reading is divided by 4.

2. *Gravimetric Method.*—This depends upon the reducing action of lactose upon alkaline copper tartrate solutions, the weight of Cu_2O formed being a function of the weight of lactose present. Tables of weights of sugars corresponding to given weights of Cu_2O may be found in any of the works upon sugar analysis, food analysis, and kindred subjects.

The solutions used is Soxhlet's modification of Fehling's solution, made as follows:—

1. $CuSO_4.5H_2O$, 34·639 grms. dissolved in water and made up to 500 cc.

2. $KNaC_4H_4O_6$ (Rochelle salts), 173 grms. and sodium hydroxide 50 grms. made up to 500 cc.

These solutions are mixed volume for volume just before use.

3. A half normal solution of NaOH.

25 cc. of milk are diluted with 400 cc. of water, 10 cc. of above described copper sulphate solution and 8·8 cc. of the half normal sodium hydroxide solution added. The mixture must be acid at the point and still contain copper in solution. The whole is then diluted to exactly 500 cc., mixed thoroughly, and filtered through a dry paper.

Lactose is now determined upon aliquot parts of this solution as follows:—

Fifty cc. of the mixed copper reagent (half-and-half of copper sulphate and Rochelle salts solutions) are heated to boiling, 100 cc. of the prepared sugar solution added, and the whole boiled for six minutes. The red precipitate of Cu_2O is thrown on a tared Gooch crucible, washed with hot water, then with alcohol, finally with ether, and dried to constant weight at 100°C. Weight $Cu_2O \times 0\cdot8883$ = weight Cu.

From the weight in mgrms. of Cu, the corresponding weight of lactose is taken from the table, which may be found in any work upon commercial organic analysis, food analysis, or from *Bull.* 107, U.S. Department of Agriculture.

$$\frac{25 \text{ cc.} \times \text{sp. gr.}}{5} = \text{weight sample of milk.}$$

$$\frac{\text{Wt. of lactose (from table)}}{\text{Wt. sample}} \times 100 = \text{per cent lactose.}$$

Bacterial Count.—No milk analysis is complete without a count of the bacteria. For this purpose 1 cc. of the sample is measured into a sterile flask with a sterile pipette, and diluted to 500 cc. with sterile water. One cc. of this solution is taken in a fresh pipette and again diluted to 100 cc.

Six tubes of nutrient agar are placed in hot water, the agar melted, and then allowed to cool to 40° C.

One cc. of the low dilution is placed in each of three

sterile Petri dishes, properly marked. Three samples of the high dilution are similarly prepared. The agar from the tubes is then poured into the dishes, care being taken to allow as little exposure to the air as possible, and the solution and agar mixed by gently flowing the contents of the dish back and forth. The agar is allowed to set and the dishes are then inverted and incubated at a temperature of 38° C. for twenty-four hours, when the number of colonies is counted in each.

Average of counts for the first dilution multiplied by 500 gives bacteria per cc. of the original milk, and for the second dilution the number of colonies is multiplied by 50,000.

THE SCIENTIFIC WEEK.

(From Our Own Paris Correspondent).

Notes on Henri Poincaré.

Prof. Paul Appel, Dean of the Faculty of Science, has just published a notice on Henri Poincaré in the *Scientific Bulletin* of the University of Paris. Poincaré, says Prof. Appel, studied at the Lycée or Public School of Nancy. He was an excellent pupil, whose intelligence, sagacity, and instructive mind were at an early age remarked by his masters. He passed the examination for the degree of Bachelor of Arts on August 5th, 1871, with the note "good." He was received Bachelor of Science on November 7th, 1871.

M. Floquet, the present Dean of the Faculty of Science of Nancy, has communicated the official report of this examination to M. Appel. In this report it is seen that Henri Poincaré obtained to note 0 for the written composition of physics and the note 2 (out of a maximum of 5 points) for the written composition of mathematics. Undoubtedly, says M. Appel, this 0 and this 2 will be noticed a little maliciously. The eminent physicist, mathematician, and philosopher, Henri Poincaré, was, indeed not very brilliant in his examinations. The fact is not of a nature to diminish our scepticism concerning the examination for the Bachelor's degree.

At the end of 1873 Poincaré won the first prize for mathematics at the general competition of all the Parisian Boys' Colleges; he was received first at the competitive examinations for the entry to the Polytechnic School, and fifth for the Higher Normal School. This last fact, joined to the plucking of Galois, the young French mathematician, who died at the early age of 24 years, and who failed to pass the entry examination to the Polytechnic School, was also not of a nature to diminish the scepticism of the learned men concerning competitive examinations — artificial proofs whose results are often belied in after life.

Action of Chloride of Calcium in the Curdling of Milk.

M. Luidet has studied the action of chloride of calcium in the curdling of raw and of cooked milk. He shows that the caseines solubilised by the elements of the serum phosphates, citrates, alkaline chlorides, lactoses, &c., lose their solubility when under the influence of chloride of calcium, the alkaline phosphates are transformed into insoluble phosphate of calcium, and the alkaline citrates are changed into citrate of calcium, in which the caseines are insoluble. Moreover, the bicalcic phosphate that is formed is dissociated in the midst of the water into tricalcic and monocalcic phosphate. This latter attacks the lime which was dissolved by the caseines and makes them more soluble, reforms some bicalcic phosphate which is dissociated in its turn, and so on until all the lime is transformed into insoluble phosphate, which is found again on the curd. The addition of chloride of calcium increases thus the quantity of curds, at the expense of the solubilised caseines in the serum, and augments the tenor of this latter in phosphate of calcium; the chloride of calcium, if too much has not been put in, will disappear, and in the curds there will only be found chloride of sodium and phosphate of calcium, which are the normal elements of cheese.

Dangers of Fire from Incandescent Lamps.

Concerning the burning of the theatre of Stettin, M. Boje has been requested to examine if the cause of the fire might not be attributed to portable electric lamps. To this intent he supplied each type of protector with lamps with carbon filaments of 16 candles, 220 volts, and by turns wrapped them in stuffs of cloth, wool, silk, and linen, so as to isolate them as much as possible from the air. A glass tube plunged in the mass rendered it possible to follow the variations of temperature in the neighbourhood of the lamp. In the case of two lamps the cloth stuff caught fire after twenty-five minutes contact with the ampullas, and after thirty minutes without touching the glass. The light woollen, silk, and cotton stuff took fire when in contact with the bulbs at the end of five to fifteen minutes. The heating was such that the ampulla itself became softened and broke. The two other lamps wrapped up in towels caused burns at the end of thirty minutes and two hours and forty minutes. The highest temperature noted was 213° C.

One lamp was experimented upon by enclosing it in a box with wooden shavings. These took fire at the end of three hours. This experiment demonstrates clearly that all portable lamps actually in use may become dangerous when they are furnished with ampulla with carbon filaments of 16 candles, 220 volts. As a counter-proof, the author has made the same trials with the same envelopes, but supplied with ampullas with metallic filaments of 16 and 50 candles. The combustion was still possible with the ampullas of 50, 32, and 25 candles; only the lamp with a metallic filament of 16 candles was unable in any case to bring about combustion. The highest temperature noted (149° C.) was observed with the No. 1 covering, and the lowest 100° with covering No. 4.

The Lighting of Paris.

"Light, light," cried Goethe when dying, and this cry uttered by the great poet on his dying bed seems to have been heard by the succeeding generations of nearly a century past. Never was the love of light so great as it has been during the last few years. After the still somewhat weak light of the fishtail burners, the electric lamp with carbon filaments made its appearance. It was considered as a great progress. But the systems of lighting were improved. The Auer mantles were a new triumph for gas lighting. The electric lamps with metallic filaments came next, and the struggle between gas and electricity continues interminably.

The lighting of the public streets has followed the progress of private lighting. At the present time the City of Paris is experimenting on two processes of lighting; one electric, the other based on the employment of compressed gas. In the Avenue de l'Opéra, lamps with staples invented by the French engineer Bardon, throw out floods of light. The carbons are replaced by electrodes of steel or made of crystallised substances. On the Place de la République and the Boulevard Raspail there are powerful lamps furnished with mantles and fed by gas under pressure. A quite recent statistic, drawn up by M. Lauriol, chief engineer of the lighting service of Paris, shows that the lighting power of the apparatus which are used for public lighting amounts to about 7,000,000 candles per twenty-four hours. The quantity of gas employed in twenty-four hours for public lighting exceeds 91,600 cubic metres. For the private service the consumption (lighting and force) amounts to 1,140,000 cubic metres. The quantities of electricity employed in twenty-four hours is 13,000 kilowatts for public lighting and 154,000 kilowatts for private lighting. The hours of most intense lighting vary according to the season. It is, however, noticed that the maximum consumption of electricity takes place about 6 o'clock in winter. The maximum consumption of gas takes place about 8 o'clock in summer.

Besides these figures enormous quantities of electricity are consumed by manufactories who produce their own currents, as well as that consumed by companies of public transport, such as the Metropolitan Underground Railway, the lines of electric tramways, and also the large stores who have their own electric installations, &c.

NOTICES OF BOOKS.

Treatise on General and Industrial Organic Chemistry. By Dr. ETTORE MOLINARI. Translated from the Second and Enlarged Italian Edition by THOMAS H. POPE, B.Sc., A.C.G.I., F.I.C. London: J. and A. Churchill. 1913.

BOTH theoretical organic chemistry and its industrial applications are treated in this book, which is a first-rate work of reference for the technical student. The economic aspects of the subject are taken into consideration, and practical ideas as to cost of production, &c., are constantly put before the student. Discrepancies between practice and theory are carefully pointed out, and the conclusions which the author has drawn relating to some disputed points are clearly stated. Metric weights and measures have been preserved in the translation, but prices are given in English currency. It is perhaps rather invidious, in view of the general excellence of the work, to point out that the use of small print and of very copious footnotes makes the reading of the book rather fatiguing, and in some cases, while the meaning is clear the translation is awkward, as, for example, in "Drink causes the direct or indirect death of about 45,000 people.

Petroleum. By Sir BOVERTON REDWOOD, Bart., D.Sc., F.R.S.E., Assoc.Inst.C.E., F.I.C. Third Edition. London: Charles Griffin and Co., Ltd. 1913.

THE third edition of this work, which is undoubtedly the most exhaustive in the English language on the subject of petroleum, has been issued in three volumes. The author has had the assistance of many distinguished collaborators, including Mr. W. H. Dalton, Mr. L. V. Dalton, Prof. V. B. Lewes, Major A. Cooper-Key, and others, in revising the text and bringing the bibliography down to date. The division into sections originally adopted is still preserved, and the book gives a comprehensive and detailed account of the sources, nature, uses, properties, and testing of petroleum and allied products, while the legislative enactments relating to the subject are reproduced in full, and with the bibliography occupy a large part of the third volume.

Elementary Agricultural Chemistry. By HERBERT INGLE, B.Sc. Second Edition. London: Charles Griffin and Co., Ltd. 1913.

THIS book will be found a useful introduction to the study of scientific agriculture by those whose knowledge of chemistry is very limited. A short summary is given of the principles of inorganic chemistry, which is as complete and clear as can reasonably be expected in view of the magnitude of the subject and the very limited amount of space which can be devoted to it. The author has had a specially wide experience of agricultural work in South Africa, and pays a good deal of attention to the problems and conditions met with there and in sub-tropical and tropical regions generally, so that Colonial readers and future colonists may find the book better suited to their needs than a text-book based upon English or European practice only. The second edition has been thoroughly revised, and a few errors and omissions have been rectified.

Industrial Poisoning. By Dr. J. RAMBOUSEK. Translated and Edited by THOMAS M. LEGGE, M.D., D.P.H. London: Edward Arnold. 1913.

MUCH work on industrial poisoning has been done on the Continent, and the author of this book has a very extensive knowledge of the subject, which he has now placed at the disposal of the public. The scope of the book is wide, and in the words of the preface it is "intended for all who are, or are obliged to be, or ought to be interested in industrial poisoning." Short accounts are given of various processes which are known to have injurious effects upon the health of the workers engaged in them. Some important recent cases are discussed, with full particulars, but the text is not overloaded with historical facts. The symptoms of poisoning by different agents are described, and preventive measures are very comprehensively treated, while social and legislative precautions taken in Germany and elsewhere are given full consideration. The translating and editing has been efficiently performed, and the translator has added some useful notes.

CORRESPONDENCE.

SOME CURIOUS ATOMIC WEIGHT RELATIONS.

To the Editor of the Chemical News.

SIR,—Several years ago I pointed out some curious relations between the atomic weights of argon, iron, bromine, and silver (CHEMICAL NEWS, c., 37). It may be of some interest to note that the same characteristic relations may be extended to a similar series of elements, which leads one to the supposition that an inactive gas, of atomic weight 9·75, exists.

The following table shows such an extension:—

At. wts.	Differences.		At. wts.	Differences.	
[Ar = 39·9]					
	—— 0				
		—— 16 (c)			
Ar = 39·9			(?) = 9·75		
	—— 16			—— 49·25	
		—— 8 (b)			—— 18·6 (b_1)
Fe = 55·9			Co = 59·00		
	—— 24			—— 67·92	
		—— 4 (a)			—— 9·3 (a_1)
Br = 79·9			I = 126·92		
	—— 28			—— 77·25	
Ag = 107·9			Tl = 204·17		

$$2a = b;\ 2b = c. \qquad 2a_1 = b_1.$$
$$a + b + c = 28. \qquad a_1 + b_1 = 28.$$

Notes.—The intervening active elements between argon and iron = 6 or 7; between iron and bromine = 8; between bromine and silver = 9. Similarly, the elements between "9·75" and cobalt = 20 or 21; between cobalt and iodine = 22 or 23; between iodine and thallium = 24 or 25. Uncertainty exists as regards the exact number of intervening elements, or the numerical or chemical order that should be observed in counting some of them. The value "9·75" was arrived at by a curve method described in the citation above. The continuation of the right-hand series would lead to an argon analogue of atomic weight about 21·7. The above atomic weight values of the known elements are in practical agreement with the present experimental values. Not knowing the exact values of the decimal fractions of a_1 and b_1, the idea of the greatest possible symmetry in these values, relative to the whole numbers, is shown by giving them the repeating characteristics indicated, which is obviously in accordance with the scheme of geometrical progression involved.

The significance of these relations rests partly upon the close similarity of the parallel elements. The nearest related element to iron is undoubtedly cobalt. Similarly,

bromine has its nearest higher analogue in iodine. Silver is more difficult to match in the same way, but from the following considerations thallium is perhaps eligible for the place. I will quote respectively from (1) Bloxam's "Chemistry," 1895, p. 432; (2) Senter's "Inorganic Chemistry," 1911, pp. 472—473; (3) Mellor's "Modern Inorganic Chemistry," 1912, p. 637:—(1) . . . "But thallium appears to be more nearly related to another monatomic metal, silver, by the sparing solubility of its chloride and the insolubility of its sulphide." (2) "The thallous salts resemble those of the alkalis, inasmuch as the hydroxide and carbonate are soluble in water, whilst the relatively slight solubility of the thallous halides recalls the silver halides. In its trivalent compounds thallium resembles aluminium and gold . . . thallic iodide, TlI_3 . . . is isomorphous with the tri-iodides of rubidium and cæsium." (3) "The physical properties of the metal (thallium) closely resemble lead, and its compounds are related to aluminium, gallium, and indium, much as gold is related to the alkali metals, and mercury to zinc and cadmium. Thallium forms a series of thallous salts similar in properties to mercurous and silver salts. The thallic salts are not very stable, and they behave somewhat like the auric salts."

Mention should be made of the work of Tutton (*Proc. Roy. Soc.*, Nov. 25, 1909, abstracted in Chemical News, c., 298) "On the Relation of Thallium to the Alkali Metals."

From the above it will be seen that the introduction of thallium in the special series here shown is not purely an arbitrary procedure.

There is probably no final and absolute system of classification that is satisfactory from all points of view, therefore different special groupings should be studied, as they may lead to a better understanding of elemental relations.

A letter of mine in the Chemical News (cvii., 311), and the papers referred to therein, have a bearing on the inactive elements of low atomic weight indicated by the above scheme.—I am, &c.,

F. H. Loring.

(P.S.—The alkali metals stand next to the inactive gases, and, if thallium is allied to the former, its neighbouring element, mercury, should have some properties in common with the latter. This is the case in so far as Thomson's "positive ray" experiments bring mercury into line with the argon gases. Mercury is comparatively inert when its liquid state is taken into account, as soft metals are usually very active chemically).

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Academie des Sciences. Vol. clvi., No. 22, June 2, 1913.

1-Benzoyl-2-Phenyl-Δ_1-Cyclopentene.—Edouard Bauer.—When sodamide acts upon 1-benzoyl-2 phenyl-Δ_1-cyclopentene the reaction is the same as with benzophenone. Two sets of crystals are obtained, one melting at 135° and the other at 23°. The former are the amide of 2-phenyl-Δ_1-cyclopentene-1-carbonic acid, the other product being benzene, while the crystals melting at 23° are 1-phenyl-Δ_1-cyclopentene.

Researches on Carpiline.—E. Léger and Ferdinand Roques.—When carpiline is heated to 140° with water in sealed tubes for ten hours two new bases are obtained, one soluble and the other insoluble in cold water. The former is Pyman's pilosinine, and the latter anhydropilosinine. Pyman supposes that carpiline has a constitution like that of pilocarpine, the group C_6H_5—CHOH— replacing the C_2H_5 group of pilocarpine. Probably it contains the group C_6H_5—CHOH—CH, which, under the influence of heat, splits into C_6H_5—COH and CH_2. At the same time by the loss of water it gives the group C_6H_5—CH=C, which is present in anhydropilosine.

Berichte der Deutschen Chemischen Gesellschaft. Vol. xlvi., No. 8, 1913.

Activation of Chlorate Solutions by Osmium.—K. A. Hofmann, O. Ehrhart, and Otto Schneider.—Traces of osmium tetroxide convert neutral chlorate solutions into strong oxidising agents, and the authors' experiments show that this action is due to the addition of chlorate to the osmium tetroxide and the formation of a substance of high oxidation power.

Preparation of Molybdenum and Tungsten Carbides.—Siegfried Hilpert and M. Ornstein.—Molybdenum and tungsten carbides can be obtained by treating the powdered metals with methane or carbon monoxide at high temperatures. The limits of the absorption of carbon correspond to simple stochiometric proportions. In the case of molybdenum the limiting values correspond to Mo_2C for 600° and 1000°. At 800° the composition varies between MoC and Mo_2C_3. Tungsten is converted into W_3C_4 by carbon monoxide at 1000°, and at 800° by methane-hydrogen (1:1) into the carbide, WC. The carbides are also obtained if the trioxides are used instead of the metals.

Mutual Expulsion of Metals from their Phenyl Compounds.—Siegfried Hilpert and Gerhard Grüttner.—By simple replacement of mercury in organic compounds alkyl derivatives of beryllium, magnesium, aluminium, zinc, and phenyl derivatives of magnesium and aluminium can be obtained. Cadmium exhibits only a very slight tendency to form organic compounds, although the authors have obtained cadmium diphenyl $Cd(C_6H_5)_2$. Magnesium halogen alkyls can be used to prepare compounds of less electropositive metals, such as tin, lead, and mercury. The sensitiveness of phenyl compounds towards air and water increases with increasing atomic weight and increasing electronegative character of the metal in question.

Arsenious Compounds.—A. Michaelis and Arthur Schäfer.—The compounds of arsenic often possess a higher molecular weight than the corresponding nitrogen compounds. In order to see whether this held good for arseno-benzene and arseno-toluene the authors determined their molecular weights (the former by the rise of the boiling-point of a benzene solution, and the latter by the lowering of the freezing-point of a phenol solution). The formulæ were thus found to be $C_6H_5.As:As.C_6H_5$ and $C_7H_7.As:As.C_7H_7$ respectively, and the arsenious compounds are the true analogues of the azo-compounds.

Determination of Nitric Oxide and Oxygen Gasometrically.—Gabriel Klinger.—Nitrogen trioxide is formed when nitric oxide comes into contact with oxygen or air, and in presence of caustic potash potassium nitrite is formed. Oxygen can be determined by means of nitric oxide, or the latter by means of oxygen by passing the one gas into a pipette containing *dry* potash, then introducing the other gas, and after a few seconds determining the absorption by the KOH. The equation is $4NO + O_2 = 2N_2O_3$, and thus four-fifths of the contraction represents the NO and one fifth the oxygen.

Calcium Boride.—E. Wedekind.—Calcium boride can be prepared by heating a mixture of finely-powdered calcium borate and metallic calcium (3 : 5) in a vacuum. The boride thus obtained is a crystalline light brown powder of sp. gr. 2·11. It conducts electricity, and electrodes made of it undergo partial oxidation, giving a mass which is as hard as diamond. It is partially oxidised when heated in air. It is stable towards acids (with the exception of nitric acid), and also towards liquid alkalis, but is decomposed when fused with potash or soda.

THE CHEMICAL NEWS.

VOL. CVIII., No. 2805.

THE INFLUENCE OF CHLORINE ON THE DETERMINATION OF NITRATES BY THE PHENOL DISULPHONIC ACID METHOD.

By ROBERT STEWART and J. E. GREAVES.

THE question involved in this study is of fundamental importance in the determination of nitrates in cultivated soils of the arid west, which may be impregnated with alkali. Earlier work at this laboratory on this question demonstrated a marked influence of chlorine upon the amount of nitrates found (Stewart and Greaves, *Journ. Am. Chem. Soc.*, 1910, xxxii., 756). Thus, it was found that if the soil solution contained even as low a concentration as 2·6 parts per million of chlorine in the soil extract less nitrates were found by this method than were actually present.

The experimental data recently presented by Lipman and Sharp (*Univ. of Cal. Publication in Agr. Sci.*, 1912, i., 12), although they are apparently not aware of this fact, confirm this conclusion. This may be seen by converting the results obtained in both cases to the same basis in order to make a comparison, since our results are reported as parts per million of chlorine in the *soil extract*, while Lipman and Sharp's results are reported as milligrms. of sodium chloride present.

The results converted to the same basis, *i.e.*, milligrms. of sodium chloride actually present in the portion of the solution used, are compared in Table I.

TABLE I.—*Influence of Ionic Chlorine on the Determination of Nitrates in Solution.*

By Stewart and Greaves.

Mgrm. NaCl.	Nitric nitrogen added.	Nitric nitrogen found.	Nitric nitrogen found (per cent).
0·04	0·01	0·01	100
0·09	0·01	0·01	100
0·13	0·01	0·01	100
0·27	0·01	0·009	90
0·52	0·01	0·0094	94
0·79	0·01	0·0086	86

By Lipman and Sharp.

NaCl.	Nitric nitrogen added.	Nitric nitrogen found.	Nitrogen found (per cent).
0·01	0·05	0·051	102
0·05	0·05	0·051	102
0·10	0·05	0·049	98
0·25	0·05	0·045	90
0·50	0 05	0·041	82
1·00	0·05	0·035	70

Thus, it may be readily seen that when only 0·1 mgrm. of sodium chloride was present in both cases all of the nitrates present could be easily determined. Lipman and Sharp, however, found that when 0·25 mgrm. of sodium chloride was present, that only 90 per cent of the nitrates actually present could be determined, while we found that when 0·27 mgrm. of sodium chloride was present, only 90 per cent of the nitrates could be found. With a concentration of 1 mgrm., Lipman and Sharp found only 70 per cent of the nitrate, while we, with 0·79 mgrm. of sodium chloride, found only 86 per cent of the nitrate. It is thus seen that Lipman and Sharp have confirmed, in a remarkable manner, the results obtained at this laboratory. It is seldom that investigators in separate laboratories get such concordant results. It is thus fully confirmed that ionic chlorine has a marked influence on the determination of nitrates in the soil extract, and that in alkali soils this fact must be taken into consideration in determining the nitrate content.

There is still another phase of this question, however, one which, so far as we are aware, has never been considered by previous investigators, and this is the influence of chlorine, which is not in the ionic form but is combined in the organic molecule, on the determination of the nitrate content of the soil extract. This is a question of considerable practical importance, since chloroform is frequently used to inhibit the action of bacteria in the soil extract. Especially is this so in case of the use of the lime method as proposed by Lipman and Sharp. In the use of this method, if chloroform be also used, it appeared to us that there is the possibility of the formation of ionic chlorine from the organic chlorine of the chloroform, and if present in sufficient quantities this would materially affect the value of the results obtained. The assumption that ionic chlorine would be formed by the action of calcium oxide on the chloroform seemed to be justified by the fact that is so well known, that potassium hydroxide does act on chloroform as indicated in the following equation: $CHCl_3 + KOH = HCOOK + 3KCl + 2H_2O$, with the production of ionic chlorine. This being the case why may not calcium hydroxide act in a similar manner, as follows: $2CHCl_3 + 4Ca(OH)_2 = (HCOO)_2Ca + 3CaCl_2 + 4H_2O$?

If such a reaction did take place, the ionic chlorine formed would materially interfere with the determination of the nitrates. In view of the fact that we are aware that chloroform is used by some investigators with the lime method, it appeared to us that the question should be exhaustively studied.

Therefore, varying amounts of chloroform were added to solutions containing 1 mgrm. of nitric nitrogen and 1 grm. of lime. These solutions were carefully worked up in a mortar, placed in a closed container, and allowed to stand over night. A portion of the solution was used the next morning to determine the ionic chlorine present, while in another portion the nitric nitrogen was determined. The results obtained are given in Table II.

An examination of the data presented in Table II. brings out two very important facts. First, that ionic chlorine is liberated when lime and chloroform are mixed together, and that the quantity of chlorine liberated varies with the chloroform. Second, that the ionic chlorine formed interferes very greatly with the accurate determination of nitrates by the phenol disulphonic acid method. It may, therefore, be seen that determinations made by this method, where the solution has both chloroform and lime present, give results which may be less than one-half of what they should be.

TABLE II.—*Influence of Chloroform on Determination of the Nitric Nitrogen by the Lime Method.*

Sample No.	Lime added.	Chloroform added. Cc.	Nitric nitrogen added. Mgrm.	Nitric nitrogen found. Mgrm.	Per cent loss.	Ionic chlorine found, mgrms. sodium chloride.
1.	1·0	none	1·0	1·0	none	none
2.	1·0	0·1	1·0	0·54	46	2·0
3.	1·0	0·2	1·0	0·37	63	5·2
4.	1·0	0·3	1·0	0·47	53	8·6
5.	1·0	0·4	1·0	0·24	76	11·4
6.	1·0	0·5	1·0	0·23	77	12·8
7.	1·0	0·6	1·0	0·37	63	16·3
8.	1·0	0·7	1·0	0·44	56	26·3
9.	1·0	0·8	1·0	0·32	68	32·0
10.	1·0	0·9	1·0	0·40	60	37·9
11.	1·0	1·0	1·0	0·40	60	41·3

As a further check on the influence of chloroform on the determination of nitric nitrogen, a great number of determinations were made on solutions containing varying amounts of nitric nitrogen, both with and without the

addition of chloroform. In the case where chloroform was added, a few drops were shaken into the solution, just as is the case where it is added to prevent bacterial action while the solution is standing. The results are given in Table III.

Table III.—*Determination by Lime Method of Nitric Nitrogen Present in Solution to which Known Amounts of Nitrate was Added.*

Sample No.	Nitric nitrogen added.	Nitric nitrogen found (mgrms.). 1st trial.	2nd trial.	3rd trial.	4th trial.	Average.
		Without Chloroform.				
1.	none	none	none	none	none	none
2.	1·0	0·88	0·90	1·0	0·82	0·90
3.	1·5	1·5	1·50	1·53	1·43	1·49
4.	2·0	2·0	2·0	2·05	2·00	2·01
5.	3·0	3·0	3·05	3·2	3·15	3·10
		With Chloroform.				
1.	none	none	none	none	none	none
2.	1·0	0·29	0·32	0·40	0·55	0·39
3.	1·5	0·52	0·70	0·63	0·78	0·66
4.	2·0	0·84	1·10	0·92	1·08	0·99
5.	3·0	0·69	1·20	1·15	1·52	1·14

These results show conclusively that in the absence of chloroform concordant results were obtained by this method, and that practically all of the added nitrate could be accurately recovered. When, however, chloroform was added to the solution containing the nitrate and calcium hydroxide, it was impossible to obtain concordant results, and the amount of nitric nitrogen found had no apparent relationship to the amount of nitric nitrogen actually present. It may thus be seen that the chloroform in the presence of calcium hydroxide very materially interferes with the accurate determination of the nitric nitrogen.

The discussion so far has had to do only with the determination of the nitrates in solution. The soil factor must be considered. Accordingly, it was decided to determine the nitric nitrogen content in two soils, one a very rich hothouse soil, the other a field soil, poor in nitric nitrogen. The nitric nitrogen was determined by the lime method both with and without chloroform. The results obtained are recorded in Table IV.

Table IV.—*Comparative Determination of Nitric Nitrogen in a Soil.*

Sample No.		Soil rich in nitrates.	Soil poor in nitrates.
	Without Chloroform.		
1.	Lime 1 grm. per 50 grms. of soil	27·0	0·36
	Lime 1 grm. per 50 grms. of soil	27·5	0·36
	With Chloroform.		
7.	Lime and chloroform	22·5	0·22
8.	Lime and chloroform	22·0	0·14

Again the marked influence of chlorine is demonstrated. In the rich soil where chloroform and lime are used there is a loss of 5 mgrms. of nitric nitrogen, while in the soil poor in nitric nitrogen there is a loss of over 50 per cent of the nitrates, and, furthermore, the results obtained are not concordant.

It is seen, therefore, that the lime method is highly desirable for use in soils rich in nitrates and organic matter, since a clear solution is thus obtained and there is no interference in the determination of the nitrates, provided chloroform is not also used.

Ionic chlorine has a marked influence on the determination of the nitrates in the solution whether the ionic chlorine is derived from the chlorides of the soil or by decomposition of the added chloroform. The result obtained also indicated clearly that chloroform should not be added to the soil extract obtained by the lime method.—*Journal of the American Chemical Society*, xxxv., No. 5.

ON THE NITRILE OF FUMARIC ACID AND THE PREPARATION OF METHYL MALEATE.

By EDWARD H. KEISER and L. McMASTER.

In the synthesis of fumaric and maleic acids from acetylene by means of the iodides and potassium cyanide the nitriles of the acids were not isolated. Subsequently E. H. Keiser and J. J. Kessler (*Am. Chem. Journ.*, xlvi., 523) obtained the nitrile of fumaric acid by heating fumaramide with phosphorus pentoxide. The long slender needles that formed as a sublimate undoubtedly had the composition of fumaric nitrile. They had a pleasant odour, and when treated with alkalis gave off ammonia. In short, the behaviour of the substance was such as one would expect from a cyanide. Difficulty was experienced, however, in trying to convert the fumaric nitrile into fumaric acid. This was no doubt due to the fact that the quantities worked with were small. We have now prepared the nitrile in larger quantities, and have succeeded in converting it back into fumaramide and into fumaric acid, thus establishing, beyond all doubt, its constitution.

This conversion was found to take place readily by means of an alkaline solution of hydrogen dioxide (*Ber.*, xviii., 355), the action taking place according to the equation:—

$$\begin{matrix} CHCN \\ \| \\ CHCN \end{matrix} + 2H_2O_2 = \begin{matrix} CHCONH_2 \\ \| \\ CHCONH_2 \end{matrix} + O_2.$$

The fumaramide thus formed was then transformed into fumaric acid by warming with dilute caustic potash.

Twenty-five hundredths grm. of fumaric nitrile was treated with 25 cc. of a 3 per cent solution of hydrogen dioxide, and the liquid made faintly alkaline with a few drops of caustic soda solution. There was a rapid evolution of oxygen, and after a short time a white precipitate separated. This was removed by filtration, and was found to be insoluble in cold water, in alcohol, and ether, but was soluble in hot water, thus showing the properties of fumaramide. In determining the melting-point, it became black at 232°, and melted completely at 267°. For the sake of comparison a sample of fumaramide was prepared from diethyl fumarate by the action of ammonia, and this behaved in the same way as that obtained from the nitrile. The melting-point of fumaramide is given by Curtius and Koch at 232° "with carbonisation" (*Journ. Prakt. Chem.*, xxxviii., [2], 478). Hell and Poliakow give it at about 266° (*Ber.*, xxv., 643). With a second specimen of the fumaramide made from the nitrile we found that at 233° the substance became black, and at 267° it melted sharply.

The fumaramide thus made from fumaric nitrile was then hydrolysed by warming upon the water-bath for one hour with dilute caustic potash. All odour of ammonia was then gone, and the solution was allowed to cool, and was then neutralised with dilute nitric acid. Silver nitrate was added, and a white precipitate of silver fumarate was formed. This was filtered, washed, and dissolved in dilute ammonia, and re-precipitated by again neutralising with nitric acid. The precipitate, after filtering and washing, was dried at 100°. On analysis the following result was obtained:—

0·0628 grm. substance gave 0·0543 grm. AgCl.

Ag calculated for $C_5H_2O_4Ag_2$ ..	65·4
Ag found	65·1

The dried salt deflagrated like gunpowder when heated, this being one of the characteristic properties of silver fumarate. It was also insoluble in boiling water, a fact which distinguishes it from silver maleate.

Another portion of fumaramide made from the fumaric nitrile by means of hydrogen dioxide was saponified by alcoholic potash. As the amide is only slightly soluble in absolute alcohol, the solution was boiled for sixteen hours. It was then filtered and evaporated to remove the alcohol, water added, and the alkali neutralised with nitric acid.

The silver salt was then precipitated, washed, dried, and analysed.

0·1016 grm. substance gave 0·0877 grm. AgCl.

Ag calculated for $C_4H_2O_4Ag_2$ ..	65·4
Ag found	65·0

Dimethyl Maleate.—This ester has heretofore been made by the action of methyl iodide upon silver maleate. We have succeeded in preparing it from methyl alcohol, maleic acid, and sulphuric acid. Five grms. of maleic acid, 50 cc. of methyl alcohol, and 2 cc. of concentrated sulphuric acid were boiled for four hours under an inverted condenser. The liquid was then poured into an evaporating dish, and the alcohol allowed to evaporate. The residue was stirred up with barium carbonate, and allowed to stand in contact with it for several days. Ether was added to the mixture, and the solid matter separated by filtration. The ether was removed from the filtrate by evaporation, and the thick oily residue, consisting of dimethyl maleate, was distilled. Its boiling point was found to be 203°. A small quantity of a solid melting at 102° was found in the condenser; this was dimethyl fumarate. That the clear distillate was dimethyl maleate was proved by adding bromine water to a portion of it. On standing a white solid crystalline compound was obtained. This was re-crystallised from its solution in ether. It melted at 102°, and had all of the properties of dimethyl fumarate.

We have also studied the action of ammonia upon dimethyl maleate. When a mixture of the ester and ammonia solution was allowed to stand several days, the oil gradually dissolved, but no precipitate of amide was formed as in the case of the dimethyl fumarate. On evaporating slowly, after the ammonia and water were removed, thick yellowish oil remained, which became semi-solid when it was stirred, and was very difficult to detach from the platinum dish in which it was contained. A portion of it, when heated, acquired a red colour. Another portion, when mixed with phosphorus pentoxide, gradually became hot, and as the mass turned black a white sublimate came off which was condensed in an inverted funnel. This sublimate melted at from 135° to 138°, and may have been the nitrile of maleic acid. A third portion was warmed with caustic soda, and ammonia was given off. In all probability this thick glue-like mass was the amide of maleic acid.—*American Chemical Journal*, xlix., No. 2.

REACTIONS OF OZONE WITH CERTAIN INORGANIC SALTS.*

By YOSHITO YAMAUCHI.

(Concluded from p. 92).

II. *Reactions of Ozone Investigated according to this Method* (continued).

4. *Thallous Nitrate.*—Schönbein first studied the oxidation of thallium or thallous hydroxide by ozone in the presence of water (*Journ. Prakt. Chem.*, 1864, xciii., 36; 1865, xcv., 470). Schöne applied this reaction to the quantitative analysis of ozone (*Ber.*, 1880, xiii., 1508), making use of test-paper soaked in thallous hydroxide solution, where the depth of the colour of the thallic oxide formed should vary according to the amount of ozone present. Lamy settled the composition of thallic oxide, dried at 100°, to be $Tl_2O_3.H_2O$ (*Ann. Chim. Phys.*, lxvii., [3], 385), while Rabe claims to have obtained the anhydrous oxide Tl_2O_3 by oxidising an alkaline solution of a thallous salt with hydrogen peroxide (*Zeit. Anorg. Chem.*, 1906, xlviii., 428).

According to the author's experiments, the water in the thallic oxide seems never to be equal to one molecule, as was shown by Lamy. So it may be urged that hydrated thallic oxide is very liable to lose its water in part even when dried below 100°. He also determined as usual the amount of thallic oxide precipitated equivalent to the ozone used, from the results of which the equation for the reactions could be well established.

An ammoniacal solution of thallous nitrate was taken for the purpose of experiment. An aliquot portion, after being introduced into the tube containing ozone, was shaken vigorously for a few minutes only. The voluminous brown precipitate was then washed, collected on a weighed filter, dried in an air-bath below 100°, and finally weighed. The results of the experiment are given in Table VII.

TABLE VII.

No.	Ozone, in grm.	Thallic oxide precipitated by the action of ozone, in grm.	Thallic oxide per grm. ozone, in grms.
1 ..	0·0206	0·1038	5·04
2 ..	0·0151	0·0618	4·09
3 ..	0·0201	0·0952	4·74
4 ..	0·0147	0·0750	5·10
5 ..	0·0139	0·0716	5·15
6 ..	0·0182	0·0857	4·71
7 ..	0·0139	0·0635	4·57
		Mean	1 : 4·77

If the reaction be represented as follows:—

$$2TlOH + 2O_3 = Tl_2O_3 + H_2O + 2O_2 \quad . \ . \ 10,$$

and the oxide be considered to retain no water at all, then the ratio of ozone to the oxide formed is 1 : 4·76, in good accord with the experimental data.

Now, in the hope that the composition of thallic oxide might be better established, the author converted 0·5096 grm. of well dried oxide into thallic chloride, added a certain quantity of potassium iodide, and then determined the amount of iodine liberated from it. The amount of thallium equivalent to iodine was calculated from the equation—

$$TlCl_3 + 3KI = TlI + 3KCl + I_2 \quad . \ . \ . \ 11,$$

and then re-calculated to thallic oxide, Tl_2O_3, with no water, as 0·4970 grm. The loss of weight from the original 0·5096 grm., about 2·4 per cent, may be due to some quantity of water still retained.

That the oxidation of a thallous salt by ozone goes on rapidly and completely, and that the thallic oxide thus formed can be very easily weighed, affords surely another very convenient method for the gravimetric determination of ozone in contrast to that of Schöne (*loc. cit.*). It is then only necessary to take proper care to dry the oxide always at a constant temperature, in order to have the water regularly expelled.

5. *Mercurous Nitrate.*—According to Mailfert (*Comptes Rendus*, 1882, xciv., 860), mercurous salts in solution are easily oxidised by ozone partly to mercuric salts, which go into solution, and partly to basic salts, which remain undissolved.

The author examined the action of ozone on mercurous nitrate in the presence of an excess of nitric acid, and found that the oxidation takes place, though very slowly and incompletely, there remaining always some odour of ozone. The formation of basic salts was not perceived, because there was present much excess of nitric acid.

The amount of the mercuric salt formed was determined from the quantity of the unchanged mercurous salt remaining, which was precipitated and weighed in the form of chloride. The results of the experiments are given in Table VIII.

TABLE VIII.

No.	Ozone, in grm.	Mercurous nitrate oxidised by ozone, in grm.	Mercurous nitrate per grm ozone, in grms.
1 ..	0·0100	0·0919	9·19
2 ..	0·0066	0·0614	9·30
3 ..	0·0108	0·1090	10·09
4 ..	0·0110	0·1101	10·01
5 ..	0·0090	0·0807	9·63
		Mean	1 : 9·64

* *American Chemical Journal*, xlix., No. 1.

Calculated for the equation—

$$Hg_2(NO_3)_2 + O_3 = HgO + Hg(NO_3)_2 + O_2 \quad . \quad . \quad 12,$$

the ratio of ozone to mercurous nitrate is 1 : 10·94, wherein the difference from the experimental data shows the incompleteness of the reaction.

6. *Ferrous Ammonium Sulphate* (Schönbein, *Liebig's Ann. Chem.*, 1854, lxxxix., 293, makes the statement that the ferrous salt is oxidised by ozone to the ferric state).—A solution of this salt was treated in the usual manner with ozone, and the amount of oxidised salt was determined by subtracting the unchanged ferrous salt, as determined with potassium permanganate, from the total quantity of ferrous salt originally taken. The ratio of the ozone to the oxidised salt was found from the following data:—

Table IX.

No.	Ozone, in grm.	Ferrous ammonium sulphate oxidised by ozone, in grm.	Ferrous ammonium sulphate per grm. ozone, in grms.
1 ..	0·0023	0·0332	14·43
2 ..	0·0111	0·1484	13·37
3 ..	0·0047	0·0666	14·17
4 ..	0·0064	0·0809	12·64
		Mean	1 : 13·65

Calculated for the equation,—

$$2Fe(NH_4)_2(SO_4)_2 + O_3 = \\ = Fe_2O(SO_4)_2 + 2(NH_4)_2SO_4 + O_2 \quad . \quad . \quad . \quad 13,$$

the ratio is 1 : 11·83. The difference between the experimental ratio and the theoretical must be due to the simultaneous action of ordinary oxygen, as we have seen in the case of stannous chloride.

7. *Tellurous Oxide* (*cf.* Mailfert, *Comptes Rendus*, 1882, xciv., 1186).—By passing ozone into tellurous oxide suspended in water, no appreciable amount of oxidation products could be detected.

8. *Titanium Dioxide.*—Since titanium dioxide dissolved in concentrated sulphuric acid is very easily oxidised by hydrogen peroxide, the author made certain tests as to whether it is also oxidised by ozone. The results, however, were always negative.

9. *Chloropalladious Acid.*—According to L. Wöhler and King (*Zeit. Anorg. Chem.*, 1905, xlvi., 327), oxidation of this compound by ozone takes place in the followin; manner:—

$$H_2PdCl_4 + 4H_2O + O_3 = Pd(OH)_4 + 4HCl + H_2O + O_2 \qquad 14.$$

But, as there was found no convenient way of distinction between the palladic and palladious compounds, the author could not apply his method to test the correctness of the above equation.

Summary.

1. As the concentration of ozone differs with every preparation, all methods of determining the concentration through the consumption of the gas must involve using up the preparation; *i.e.*, when the concentration is known, the preparation no longer exists. The method of its determination by direct weighing is also not convenient. The author has therefore contrived a new method of dividing one sample into two parts, and of determining the concentration of the one by measuring that of the other by analysis.

2. So far as the author could determine, ozone seems to be decomposed according to the equation $O_3 = 3O$ only in the case of the oxidation of stannous chloride. The decomposition goes on, however, usually as follows:— $O_3 = O_2 + O$.

3. The action of ozone on sodium thiosulphate has been studied by the author perhaps for the first time. There take place two reactions, in which the ozone seems first to cause the catalytic decomposition of the thiosulphate, and then to be able to effect a partial oxidation of the sulphite formed.

4. Formation of thallic oxide from a thallous salt by ozone occurs very rapidly and completely. It may surely be utilised as a gravimetric method in the quantitative determination of ozone.

THE VOLUMETRIC DETERMINATION OF GOLD.

By VICTOR LENHER.

It has been shown that sulphurous acid is capable of reducing auric chloride to aurous in the presence of certain other salts (*Journ. Am. Chem. Soc.*, 1913, xxxv., 546). Through the agency of this reagent it is possible to estimate gold volumetrically easily and accurately.

In the following work a sulphurous acid solution was prepared by evolving sulphur dioxide from sodium acid sulphite by means of hydrochloric acid, and, after washing the gas, conducting it into repeatedly distilled water. The strength of the sulphurous acid necessarily varied from time to time, due to its gradual oxidation. Its strength varied from 0·005 grm. Au to 0·002 grm. Au per cc. Sulphurous acid solution requires frequent standardisation, owing to its ability to slowly oxidise by absorbing oxygen from the air in the container and pass over into sulphuric acid. After a large amount of experimentation under widely differing conditions the idea of using a permanganate solution as a convenient standardising solution was abandoned. Working under the most favourable conditions, it has not been found possible to obtain results having an error lower than 1 per cent between permanganate and sulphurous acid.

The most reliable method of standardising sulphurous acid is through the agency of iodine. It is entirely immaterial for the methods to be described whether the sulphurous acid solution is standardised on a known weight of iodine in potassium iodide, or whether solid potassium iodide is dissolved in water acidulated with sulphuric or hydrochloric acid and a definite amount of standard permanganate introduced. As a precaution both of the methods indicated were used continuously, and in addition a gold solution whose content had been determined gravimetrically was also used as a standardisation check on the sulphurous acid solution.

1. Auric chloride when treated with potassium iodide liberates iodine according to the equation—

$$AuCl_3 + 2KI = AuCl + 2KCl + I_2.$$

The iodine thus liberated can be titrated in presence of excess of potassium iodide by means of standard sulphurous acid. Starch can be used as the indicator.

2. Auric chloride can be treated with excess of a strong solution of magnesium chloride, then with potassium iodide, and the liberated iodine titrated with sulphurous acid.

3. Auric chloride when treated with potassium bromide yields bromine thus:—$AuCl_3 + 2KBr = AuCl + 2KCl + Br_2$. The liberated bromine can be titrated with a solution of sulphurous acid.

4. Auric chloride treated with magnesium chloride and potassium bromide similarly liberates bromine, which can be titrated with sulphurous acid.

5. Auric chloride when treated with magnesium chloride gives a yellow colour, which can be decolorised by titration with sulphurous acid.

6. Auric chloride and sodium chloride give a yellow colour which by sulphurous acid can be titrated to the colourless or aurous state.

In order to test the efficiency of these principles auric chloride solutions were prepared by solution of weighed amounts of metallic gold in hydrochloric acid and potassium chlorate, and the excess of chlorine removed by the addition of ammonia until the formation of a permanent precipitate, which was then dissolved in hydrochloric acid.

Unless precautions of this character are taken the gold solution will either contain some free chlorine, on the one hand, or some metallic gold will separate on the other, when an attempt to remove the free chlorine by evaporation to dryness, or nearly to dryness, is made. Evaporation of a pure auric chloride solution, even on the water-bath, causes the production of a small amount of aurous chloride, which on subsequent dilution gradually changes to metallic gold and auric chloride. By the treatment of metallic gold with hydrochloric acid and potassium chlorate followed by the ammonia and hydrochloric acid treatment, an auric solution can be satisfactorily obtained.

Series 1.

Definite amounts of gold chloride, prepared in the manner indicated, and acid with hydrochloric acid were treated in a dilution of 100 cc. with about 3 grms. of potassium iodide, and the iodine liberated was titrated with a standard solution of sulphurous acid with the following results:—

No.	Au taken (grm.).	Au found (grm.).	Error.
1.	0·0395	0·0395	—
2.	0·0439	0·0438	−0·0001
3.	0·0878	0·0876	−0·0002
4.	0·1098	0·1092	−0·0006
5.	0·1107	0·1108	+0·0001
6.	0·2289	0·2289	—
7.	0·4395	0·4397	+0·0002
8.	0·7301	0·7302	+0·0001

Series 2.

Gold chloride solutions were treated with an excess of a saturated solution of magnesium chloride, potassium iodide was added, and the titration by means of sulphurous acid effected in a dilution of 100 cc.

No.	Au taken (grm.).	Au found (grm.).	Error.
9.	0·0439	0·0440	+0·0001
10.	0·0878	0·0879	+0·0001
11.	0·1061	0·1063	+0·0002
12.	0·2653	0·2652	−0·0001
13.	0·5305	0·5298	−0·0007

Series 3.

Known amounts of gold chloride solution were treated with excess of a saturated solution of magnesium chloride. The yellow colour of the auric chloride is considerably deepened by the addition of magnesium chloride. When sulphurous acid is added from the burette, the solution is bleached progressively until colourless. No other indicator is necessary.

No.	Au taken (grm.).	Au found (grm.).	Error.
14.	0·0439	0·0438	−0·0001
15.	0·0439	0·0440	+0·0001
16.	0·2289	0·2289	—
17.	0·2289	0·2289	—

In numbers 14, 15, and 16, 25 cc. portions of auric chloride solution containing a small amount of hydrochloric acid were treated with sufficient excess of concentrated magnesium chloride to bring the volume to 100 cc., and titrated. In No. 17 conditions were the same, except that 20 cc. of concentrated hydrochloric acid were present, showing that a considerable amount of free hydrochloric acid does not materially affect this titration of auric chloride in presence of magnesium chloride.

Series 4.

Fifty cc. of the slightly acid solution of auric chloride were brought to a volume of 100 cc. with a saturated solution of sodium chloride, and titrated to a colourless state by means of sulphurous acid.

No.	Au taken (grm.).	Au found (grm.).	Error.
18.	0·0439	0·0438	−0·0001
19.	0·2289	0·2289	—

In all of the above titrations a decided excess of alkaline salts was present, and at this point the reaction of sulphurous acid was studied on auric chloride solutions containing free hydrochloric acid, but no salts. In such a gold solution sulphurous acid not only does not show a distinct bleaching effect but metallic gold is thrown out of the solution with ease.

Series 5.

Gold chloride containing a small quantity of hydrochloric acid was brought to a volume of 100 cc., 3 to 5 grms. of potassium bromide were added, and the red colour of the free bromine was titrated to colourless by means of sulphurous acid.

No.	Au taken (grm.).	Au found (grm.).	Error.
20.	0·0439	0·0439	—
21.	0·0439	0·0440	+0·0001
22.	0·0439	0·0438	−0·0001
23.	0·0878	0·0876	−0·0002
24.	0·2289	0·2289	—

Series 6.

Auric chloride solutions were treated with 3 to 5 grms. of potassium bromide, and made up to 100 cc. with a strong solution of magnesium chloride. The red colour of the free bromine was titrated to colourless by sulphurous acid.

No.	Au taken (grm.).	Au found (grm.).	Error.
25.	0·0439	0·0440	+0·0001
26.	0·1061	0·1063	+0·0002
27.	0·2653	0·2655	+0·0002

In the application of the above methods, the gold is originally usually in the metallic form. In order to dissolve the metal either chlorine water or hydrochloric acid and potassium chlorate are convenient solvents. The excess of the oxidising agent cannot be removed by evaporation on account of the production of some aurous chloride. The free chlorine can be advantageously removed by addition of ammonia until a permanent precipitate forms, acidulating with hydrochloric acid, and heating to re-dissolve the precipitate formed by the ammonia. On cooling, 3 grms. of potassium iodide are added, and titration is effected by a standard solution of sulphurous acid, using, if desired, starch as the indicator; or, instead of using potassium iodide, the solution can be treated with potassium bromide or with excess of sodium chloride and titrated by sulphurous acid.—*Journal of the American Chemical Society*, xxxv., No. 6.

THE ACTION OF THIONYL CHLORIDE ON THE OXIDES OF METALS AND METALLOIDS.

By H. B. NORTH and A. M. HAGEMAN.

THE action of thionyl chloride on oxides of metals and metalloids has been studied but little. The first research of this nature appears to have been made by Lenher and North (*Journ. Am. Chem. Soc.*, 1907, xxix., 33), who investigated the reaction of thionyl chloride on selenium dioxide in 1907. This work was followed in 1908 by a study of the reaction on tellurium dioxide by Lenher and Hill (*Ibid.*, 1908, xxx., 738). In 1910 North (*Ibid.*, 1910, xxxii., 184) investigated the reaction of thionyl chloride on both the red and yellow varieties of mercuric oxide.

In each of the above mentioned investigations reaction was found to proceed readily at elevated temperatures, with the formation of the chloride of the metal and the corresponding production of sulphur dioxide. The reactions were carried out in sealed glass tubes.

In 1911 Darzens and Bourion (*Comptes Rendus*, 1911, cliii., 270) investigated the reaction of thionyl chloride on a number of oxides, chiefly those of rare earths. They found that with ThO_2, La_2O_3, Sm_2O_3, ZrO_2, and Cr_2O_3 the

corresponding chlorides were formed, while V_2O_5 yielded the oxychloride $VOCl_3$, and WO_3 gave a mixture of the two oxychlorides, WO_2Cl_2 and $WOCl_4$. TiO_2 gave a peculiar compound which they supposed to be a sulpho-chloride, and Gd_2O_3 gave a mixture of chloride and oxy-chloride.

It is very probable that Darzens and Bourion made no examination of the by-products formed, inasmuch as no mention was made of them and equations were not given for the reactions.

In general, the action of thionyl chloride on an oxide of a metal results in the formation of a chloride of the metal and the liberation of sulphur dioxide. This reaction can be represented by the following general equation in which "M" represents a divalent metal:—

$$MO + SOCl_2 = MCl_2 + SO_2.$$

There are cases, however, for which this type equation does not hold. For example, with a metal having two series of salts, the lower oxide, when treated with a decided excess of the reagent, gives rise to the higher chloride; hence the reagent appears to act first as a chlorinating agent and then as an oxidising agent. If "M" in the above equation represents a metal which is tetravalent as well as divalent, the reaction first proceeds as above with the formation of the dichloride; and this compound is then oxidised to the tetrachloride according to the equation—

$$3MCl_2 + 4SOCl_2 = 3MCl_4 + 2SO_2 + S_2Cl_2.$$

By combining the two equations we obtain the following:—

$$3MO + 7SOCl_2 = 3MCl_4 + 5SO_2 + S_2Cl_2.$$

In such an oxidising reaction, the by-products are always sulphur dioxide and sulphur monochloride.

All of the reactions to be described in this paper were carried out in sealed glass tubes, and with one or two exceptions a temperature of 150—200° was employed. In each experiment about 1 grm. of the oxide, carefully dried, was treated with an excess of the reagent. All of the oxides were as pure as could be obtained.

Zinc Oxide.—Zinc oxide and thionyl chloride were heated together in sealed glass tubes for several hours at 150° without any apparent change in appearance. However, when the tubes were opened considerable pressure due to sulphur dioxide was noted. The white powder was well washed with carbon disulphide, dried, and weighed. It was then dissolved in water containing a few drops of nitric acid. Determination of chlorine and zinc proved the compound to be anhydrous zinc chloride, $ZnCl_2$; hence the reaction undoubtedly proceeded according to the equation $ZnO + SOCl_2 = ZnCl_2 + SO_2$. Judging from the fine state of division, it is probable that anhydrous zinc chloride is only slightly soluble in thionyl chloride.

Cadmium Oxide.—Thionyl chloride was found to have no action on cadmium chloride in the cold, but when heated at 200° in sealed glass tubes the brown colour of the oxide gradually disappeared with the simultaneous production of a white non-crystalline compound. This proved upon analysis to be cadmium chloride, $CdCl_2$; hence the reaction proceeds according to the equation $CdO + SOCl_2 = CdCl_2 + SO_2$. It is evident that cadmium chloride, like zinc chloride, is at best only slightly soluble in thionyl chloride and liquid sulphur dioxide.

Arsenic Trioxide.—In the case of arsenic trioxide the reaction proceeds in the cold and the oxide gradually goes into solution. It was naturally thought that the reaction follows the equation $As_2O_3 + 3SOCl_2 = 2AsCl_3 + 3SO_2$. Inasmuch as arsenic trichloride is a liquid and remains mixed with the excess of thionyl chloride and liquid sulphur dioxide, a quantitative separation is difficult. Furthermore, although arsenic trichloride boils at 130° and thionyl chloride at 78°, separation by fractional distillation is difficult owing to the small quantities of material used. A single fractionation was made, however, the portion boiling below 128° being rejected and that boiling between 128° and 132° being retained. The latter was examined qualitatively, and was found to contain arsenic in the trivalent form in addition to considerable chlorine. From this it was assumed that the above equation is correct, and that arsenic trichloride was formed.

Other experiments were performed in which a decided excess of thionyl chloride was employed at a temperature of 200°, but these, upon examination in the manner described above, gave the same tests; hence they undoubtedly contained the same compound.

Antimony Trioxide.—Antimony trioxide was found to react immediately with thionyl chloride at the ordinary temperature with liberation of considerable heat. The oxide dissolved completely in the reagent, but upon cooling white crystals of antimony trichloride separated. The reaction proceeds according to the equation $Sb_2O_3 + 3SOCl_2 = 2SbCl_3 + 3SO_2$.

Other experiments were made in which a large excess of thionyl chloride was used, and the tubes were sealed and heated at 150° for several hours. Upon cooling, no crystalline deposit was formed; hence it was supposed that the excess of thionyl chloride had oxidised the antimony chloride to pentachloride according to the equation $3SbCl_3 + 4SOCl_2 = 3SbCl_5 + 2SO_2 + S_2Cl_2$; or, representing the entire reaction by a single equation, $3Sb_2O_3 + 17SOCl_2 = 6SbCl_5 + 13SO_2 + 2S_2Cl_2$. The liquid contents of the tubes were examined carefully and were found to contain pentavalent antimony, sulphur dioxide, and sulphur monochloride; hence the authors are confident that the reaction proceeds according to the equations given above. No attempt was made to separate the products quantitatively.

Bismuth Trioxide.—Bismuth trioxide, in contrast to arsenic and antimony trioxides, was unattacked by the reagent at the ordinary temperature, but after heating for several hours at 150—200° the formation of small white crystals was noted. These crystals analysed to $BiCl_3$; hence reaction proceeds according to the equation $Bi_2O_3 + 3SOCl_2 = 2BiCl_3 + 3SO_2$.

Ferric Oxide.—Although ferric oxide is not at all attacked by thionyl chloride at the ordinary temperature, when heated at 150° the reaction proceeds readily with the formation of anhydrous ferric chloride in large green hexagonal plates, which by transmitted light are red in colour. The reaction evidently proceeds as follows:— $Fe_2O_3 + 3SOCl_2 = 2FeCl_3 + 3SO_2$. Judging from the size of the crystals, it is evident that anhydrous ferric chloride is exceedingly soluble in thionyl chloride at elevated temperatures. In all respects the crystals appear to be identical with those obtained by the action of thionyl chloride (North and Hageman, *Journ. Am. Chem. Soc.*, 1912, xxxiv., 890) and sulphuryl chloride (North, *Bull. Soc. Chim.*, 1911, [4], ix., 646) on metallic iron.

Glucinum Oxide.—Glucinum oxide was found to be unattacked by thionyl chloride even after tubes containing the oxide and reagent had been heated at 200° for thirty hours.

Calcium Oxide and Strontium Oxide.—Neither calcium nor strontium oxide were found to be attacked by thionyl chloride at temperatures up to 200°.

Magnesium Oxide.—Magnesium oxide, which had been strongly ignited and cooled over sulphuric acid, was heated with thionyl chloride for twenty-four hours at a temperature of 150—200°. The white powder, which to all appearances had not changed, was well washed with carbon disulphide, dried, and weighed. Analysis showed it to be $MgCl_2$; hence reaction evidently proceeds according to the equation $MgO + SOCl_2 = MgCl_2 + SO_2$.

Two other samples of magnesium oxide, which were tested without previous blasting, were found to react readily at slightly elevated temperatures, due, undoubtedly, to the presence of considerable magnesium hydroxide.

Silver Oxide.—Silver oxide was found to be unattacked by the reagent in the cold, and even after heating for several hours at 150° reaction had apparently not taken place, inasmuch as the brown powder appeared to be unchanged. The tubes were opened, the brown powder was

well washed with carbon disulphide, dried, and examined qualitatively. It was found to contain a trace of silver chloride. It is possible that the reaction proceeded to a slight extent and that the silver chloride formed, due to its insolubility in the reagent, served to protect the remainder of the oxide.

Cupric Oxide.—Cupric oxide was not attacked by the reagent at the ordinary temperature, but after the tubes containing the two were heated at a temperature of 200° for several hours, they were found to contain a brownish green non-crystalline powder. This substance was washed, dried, and analysed, and was found to be anhydrous cupric chloride, $CuCl_2$; hence the reaction took place according to the equation $CuO + SOCl_2 = CuCl_2 + SO_2$.

Cuprous Oxide.—Cuprous oxide, like the higher compound, was found to react with thionyl chloride at about 200°, and the product formed was cupric chloride, $CuCl_2$. Inasmuch as the reaction is one of oxidation as well as chlorination, it was thought that it proceeds according to the equation $Cu_2O + 4SOCl_2 = 2CuCl_2 + S_2Cl_2 + SO_2$. When the tubes were opened they were found to contain sulphur dioxide and sulphur monochloride in addition to the excess of the reagent; hence the equation above is undoubtedly correct.

Aluminium Oxide, Chromic Oxide, and Tin Dioxide.—These compounds were entirely unattacked by thionyl chloride, even after being heated with the reagent at 200° for hours. This is not surprising, however, inasmuch as these compounds are little attacked by reagents in general, especially after having been highly heated.

As mentioned at the beginning of this paper, Darzens and Bourion state that chromic oxide is changed to the chloride by thionyl chloride at elevated temperatures, though they make no mention of the temperature employed. It is possible that the oxide used by Darzens and Bourion may have been made at a correspondingly low temperature, or it may possibly have contained a trace of moisture. The authors of this article have been absolutely unable to bring about even the slightest reaction between chromic oxide and thionyl chloride at temperatures up to 200°.—*Journal of the American Chemical Society*, xxxv., No. 4.

PHOSPHATIC FERTILISERS.*

By Prof. W. PALMAER.

In order to meet the ever growing demand of agriculture for phosphate fertilisers, chiefly the following preparations are at present produced:—Acid phosphate, basic slag, bone meal, bicalcic phosphate, which are here given in the order corresponding to the amount produced, acid phosphate being the phosphate fertiliser most largely produced, the annual output amounting to about 10,000,000 tons.

Bicalcic phosphate so far has been produced only in small quantities, the production in Germany and France, for instance, during 1910, amounting to about 5000 tons for each country. To date this product has been obtained only as a by-product in the manufacture of glue, *i.e.*, in the process when bone is soaked in diluted hydrochloric acid, whereby the main product in the manufacture, the glue substance, remains undissolved, while a solution of bone phosphate is obtained as a by-product. This is turned to account by precipitation with lime, by which means bicalcic phosphate is obtained.

On the other hand, it is a long while ago since it was first proposed to obtain bicalcic phosphate as the chief product from every kind of raw phosphate in the same way, viz., by extracting the raw phosphate with hydrochloric acid and precipitating the solution thus obtained with lime. This method would have the advantage that one could make use of very poor and otherwise valueless raw phosphate, provided it does not contain too large a proportion of any useless soluble compound, such as carbonate of lime. In the production of acid phosphate, on the other hand, one can not utilise raw phosphate with a lower percentage than about 50 per cent bone phosphate, since owing to the admixture of gypsum the percentage in the acid phosphate of available phosphoric acid is only about half that of the raw phosphate's percentage of phosphoric acid, and consequently consideration of freight charges for the prepared article excludes the use of a raw material in which the percentage is low.

However, it has been found that the price of hydrochloric acid has been too high for the adoption of this method. This in its turn is due to the fact that the production of hydrochloric acid according to the old methods entailed the sacrifice of sulphuric acid.

But the case is different if the acid is produced in such a way that a suitable salt, for instance, perchlorate of sodium, is electrolysed with a diaphragm, so that free acid is generated in the anode chamber and a solution of caustic alkali in the cathode chamber. With an electrolysing tension of 4½ volts and 80 per cent current efficiency it is easy to calculate that in order to produce the kilogrm. equivalent of acid 182 horse-power hours are required, whereby the alkali necessary for the precipitation of the bicalcic phosphate is obtained at the same time without additional cost in the cathode chamber. If we assume that one electric horse-power can be obtained for 10 dols. a year—the usual price in many parts of Europe, and presumably in many places in America—then the cost of the equivalent of 1 kilogrm. of acid amounts to about 24 cents, the alkali being obtained at the same time; while with the old method lime had to be purchased. There is no outlay for material beyond what is caused by spilling, &c., as the electrolyte regenerates, as will be seen from what follows.

If we assume that the price of 1 ton of chamber acid with 65 per cent H_2SO_4 is 5 dols., we shall find that the cost of the kilogrm.-equivalent of H_2SO_4 (49 kgrms.) is about 38 cents.

This calculation consequently shows that provided the remaining outlay for the electrolytic process can be kept within reasonable limits, it should be assured of success, especially as it allows of the utilisation of otherwise valueless raw phosphate or refuse.

This calculation was the basis of my investigations, the object of which was consequently to try to make the method economically feasible, chiefly by finding a suitable electrolyte, and by constructing a serviceable electrolyser.

As in the process there is no consumption of chemicals, beyond loss by spilling, &c., the cost of the sulphuric acid used in producing acid phosphate is replaced by the cost of the electric power. The economic result of the method depends therefore in the first place on the price of the power.

Before entering upon detailed descriptions a general survey of the method will be of advantage.

General Features of the Method.

In an apparatus expressly constructed for the method, a solution of chlorate or perchlorate of sodium is electrolysed. In the anode chamber an acid is thereby generated —chloric or perchloric acid—and in the cathode chamber a solution of caustic soda. The electrolysis is continued until a certain quantity of the dissolved salt has been separated into acid and alkali. The anode and cathode solutions are led off into separate receivers. The acid anode solution is then allowed to work in a dissolving battery upon raw phosphate, in which process the phosphate is dissolved. Into the solution thus obtained the alkaline cathode solution is introduced, the whole being meanwhile kept vigorously stirred, until the liquid bears evidence of a slightly acid reaction; to obtain that result about half the cathode solution is required. In the process bicalcic phosphate is precipitated as a finely crystalline precipitation, which is drained off by filtration and washed. The filtrate, which contains one-third of the lime originally

* Paper presented at Eighth International Congress of Applied Chemistry. From the *Chemical Engineer*, xviii., No. 1.

dissolved, but hardly any phosphoric acid, now has added to it the remainder of the cathode solution, which has previously been saturated with carbonic acid from fuel gas. The lime is precipitated as carbonate, which is allowed to settle. The solution remaining above it is then drawn off. The original electrolyte is regenerated by its means, and again enters the electrolysing apparatus.

Of course the hydrogen, obtained as a by-product at the cathode in the electrolysis of the salt solution, could be used for making ammonia or in any other way, thus increasing the value of the products obtained.

The Nature of the Electrolyte.

With reference to the electrolyte, the salt used should be of such a nature that its acid may yield, in conjunction with lime, an easily soluble salt and of a kind which is not subject to change during electrolysis.

As electrolytes, solutions of perchlorate of sodium or chlorate of sodium are suitable, or else mixtures of those salts, the presence in small quantities of other salts, for instance, chlorides, being of no account. Both these salts can now, since they are being produced by electrolysis, be had at reasonable prices. Nitrate of sodium cannot be used because it is too strongly reduced at the cathode to nitrite, ammonia, &c.

Perchlorate of sodium is an ideal electrolyte for the purpose in question. On electrolysing its solution with a diaphragm, sodium hydrate is formed in the cathode chamber, and perchloric acid in the anode chamber, while hydrogen is developed at the cathode and ozonic oxygen at the anode. No noticeable reduction of the salt occurs at the cathode, nor any other change, and the solution of perchloric acid obtained is perfectly constant at such temperatures as occur in the electrolysing (maximum, 50° C.). Furthermore, the salt is exceedingly easily soluble (deliquescent), and thus easy to wash away.

Chlorate of sodium is less constant in that the chloric acid solution formed in the anode chamber already begins to decompose at 40° C., free chlorine being developed. Moreover, it is considerably reduced at the cathode to chloride. But the principal change is that the development of oxygen at the anode almost ceases, because the chlorate there is oxidised to perchlorate. For this reason a start can very well be made with chlorate of sodium, since, though the drawbacks mentioned (the decomposing of the chloric acid and the reduction of chlorate) appear at first, they soon disappear, viz., when the chlorate has become perchlorate of sodium. Even if you begin with chlorate of sodium, the electrolyte consists after a while of pure perchlorate, which, as has been said, suffers no further change.

The loss of perchlorate of sodium by spilling and incomplete washing need not, according to our experience, be estimated higher than at about 1 per cent of the weight of the bicalcic phosphate developed.

Another way of carrying out the process is this:—A solution of chloride of sodium is electrolysed so that a solution of caustic soda and free chlorine is obtained. The chlorine is transformed in the usual way into hydrochloric acid, wherewith the raw phosphate is dissolved, whereupon a precipitate is formed with this caustic soda. The salt is then regenerated as before. Although common salt is cheaper than perchlorate of sodium or chlorate of sodium, the process, by several reasons (depreciation of anodes, loss of chlorine, &c.), is not so advantageous.

The Electrolysis.

The electrolysis of the perchlorate of sodium solution must be carried out, as has been mentioned, in a diaphragm apparatus, and it is clear that the problem is to find a suitable anode and a suitable diaphragm. Both difficulties have been solved in a perfectly satisfactory manner, but for the present I cannot enter into details.

The voltage has been found to amount on the average to 4·5 volts per cell, including loss in connections. It varies somewhat, depending on the age of the diaphragms, the efficiency of the electrical contacts, and the temperature of the solutions, which may vary at different times of the year; but, as stated, the average voltage is 4·5. The polarisation amounts to 2·97 volts.

In a diaphragm process, where the new substances formed at the cathode and the anode remain in the solution (in this case alkali or perchloric acid), the current efficiency continually diminishes, of course, in proportion as the newly formed substances begin to take part in the current circuit. We generally produce solutions with 1 grm.-equivalent of acid or alkali per litre, and have then a current efficiency of 82 per cent and a ballast of undecomposed salt in both acid and alkali solutions.

The Raw Material and its Utilisation.

Of course, the high percentage raw phosphates used to make acid phosphate can be employed for the process, but it is not for such, but rather for low percentage raw phosphates, at present worthless or of inferior value, that the process is primarily designed. Here I need only mention in illustration low percentage apatites and apatite waste, waste from magnetic separation of phosphoric iron ore, and certain low percentage phosphorites.

As the process consists in dissolving the bone phosphate occurring in raw phosphate, and then precipitating bicalcic phosphate from the solution, the product obtained will always be of the same nature, irrespective of the percentage of the raw phosphate. We have employed raw products whose percentage of bone phosphate varied between 20 and 88 per cent.

Furthermore, the raw phosphate need not be finely pulverised, provided that the bone phosphate is not embedded in insoluble minerals and that other soluble substances, such as certain silicates, do not occur in too great a quantity. We have worked with material of as coarse crushing as 5 cm.

Assuming that the solution of bone phosphate is effected according to the formula—

$$Ca_3P_2O_8 + 6HClO_4 = 3Ca(ClO_4)_2 + 2H_3PO_4,$$

then per litre of normal acid 23·7 grms. of phosphoric acid should be dissolved. It can be foreseen, however, that the reaction in contrast, for instance, to the reaction $CaCO_3 + 2HClO_4 = Ca(ClO_4)_2 + H_2O + CO_2$ will not proceed quantitatively, since phosphoric acid is a much stronger acid than carbon dioxide. We have also found that we must reckon with a somewhat lower figure, say, 20 grms. P_2O_5 or 43·6 grms. $Ca_3P_2O_8$ per litre of normal acid. This figure holds good provided that no other bodies soluble in acids occur in the raw phosphate.

Of such, in the first place, we must take into consideration calcium carbonate, for, as we know, it readily and completely dissolves in acids. As the equivalent weight for phosphoric acid (P_2O_5) is 23·7, and for carbon dioxide (CO_2) 22, we can consequently state that 1 per cent of CO_3 in the raw phosphate causes approximately the same consumption of acid (or of energy) as 1 per cent of P_2O_5, without giving any product of any value to speak of (the amount of carbonate of lime obtained as a by-product will, of course, be correspondingly greater). A raw phosphate which contains 20 per cent of P_2O_5 (as $Ca_3P_2O_8$) and 2 per cent of CO_2 (as $CaCO_3$) consequently requires about 10 per cent more energy than a raw phosphate with the same proportion of phosphoric acid, but free from carbonate of lime.

Iron oxides (iron ores), on the other hand, are only dissolved very slightly. We found that after twenty-four hours' shaking at the usual temperature with normal acid there was dissolved of magnetite a quantity corresponding to 0·24 grm. Fe_2O_3 per litre from hematite, a quantity corresponding to 0·20 grm. of Fe_2O_3 per litre, which amounts are of no practical importance.

Most silicates are, as we know, insoluble in diluted acids. However, silicates may occur, for instance, together with apatite, which are so easily soluble that they dissolve to a noticeable degree if the acid is in contact

with them for any length of time after most of the phosphate is dissolved. Attention must be paid to this in the course of the lixiviation, and the work regulated accordingly.

As regards the utilisation of the bone phosphate in the raw material, we can as a rule count upon extracting 98 per cent of it, sometimes more, sometimes a little less, viz., when easily soluble silicate is present.

Precipitation of the Bicalcic Phosphate and Calcium Carbonate.

To precipitate the bicalcic phosphate we made use, as before stated, of the solution of caustic soda obtained by electrolysis and saturated afterwards by carbonic acid, which is introduced into the phosphate solution by means of a sprayer.

The employment of the soda solution as a precipitant, instead of milk of lime, has a considerable advantage. For the fact is that as soon as the solution has become alkaline at any point, bone phosphate is precipitated there instead of bicalcic phosphate. This once precipitated bone phosphate is only slowly converted into bicalcic phosphate, even if the average acidity of the liquid is such that only bicalcic phosphate ought to occur. At least a portion of the bone phosphate thus formed remains therefore in the precipitated bicalcic phosphate. The bone phosphate thus precipitated is very finely distributed, it is true, and is even soluble after drying in 2 per cent citric acid; but it has no fertilising value worth speaking of. The phosphoric acid precipitated as bone phosphate must therefore be looked upon as lost.

Now, it is clear that it would he much easier to avoid the formation of bone phosphate if a sodium-hydrate solution, distributed in jets, were employed as the precipitant than if milk of lime was used, since in the latter case we get particles of solid calcic hydrate, round which the solution easily becomes alkaline.

Experience also proves that in employing sodium hydrate, which is added until the phosphate solution remains very slightly acid or only just neutral, bicalcic phosphate can be precipitated so completely that only 0·1 to 0·2 per cent of all the phosphoric acid remains unprecipitated, while 98 per cent of the phosphoric acid in the bicalcic phosphate is soluble in citrate, and thus only 2 per cent of the phosphoric acid is present as bone phosphate.

The precipitated bicalcic phosphate, which is microcrystalline, is filtered off, washed, and dried. It thus forms a light pure white powder, and its proportion of citrate-soluble phosphoric acid amounts to 35 to 38 per cent, according to the completeness of the drying.

If we call to mind that about 2 per cent of the phosphoric acid in the raw phosphate is left behind in the extraction, that no quantity to speak of remains unprecipitated, and that about 2 per cent is recovered as precipitated bone phosphate, we shall find that about 96 per cent of all the phosphoric acid in the raw phosphate is extracted in the process as valuable citrate-soluble phosphoric acid.

The bicalcic phosphate obtained shows, even if it contains iron and aluminium phosphate, no falling off of soluble phosphoric acid, which is simply due to the fact that it can be perfectly dried, after which no conversion can take place. On the other hand, as we know, deterioration shows itself in damp acid phosphate. The following analyses may be quoted to show that such degeneration does not occur:—

	Total P_2O_5 per cent.	Citrate-soluble in P_2O_5 per cent.	Citrate-soluble in P_2O_5 in per cent of total P_2O_5.
Fresh	35·45	34·58	97·54
After 3 months	36·02	35·13	97·53
After 6 months	36·54	35·72	97·95

From the filtrate of the bicalcic phosphate is precipitated, as we have already mentioned, the lime that remains in the solution, together with the rest of the sodium hydrate solution, after the latter has been saturated with carbonic acid from fuel gases as carbonate of lime, which can be used as a fertiliser or in chemical workshops.

Its mass corresponds to about one-fourth of the weight of the bicalcic phosphate obtained, if the raw product used be free of carbonate. If calcium carbonate occurs in the raw product, the mass obtained in the process will be proportionately increased.

Power Expenditure.

From the statements given above it is easy to calculate what electric horse-power (direct current) produces per year of $350 \times 24 = 8400$ hours; it will work out at 2·24 tons of bicalcic phosphate with 35 per cent of citrate-soluble phosphoric acid, if free of carbonate. If a 38 per cent article is produced, $\frac{2\cdot24 \times 35}{38} = 2\cdot06$ metric tons per horse-power year will be obtained, &c. The production with carbonaceous raw product has been stated above.

Value of Bicalcic Phosphate Fertiliser.

Careful experiments extending over many years have been made, partly by Prof. H. G. Söderbaum, Agricultural Chemist at the Central Institution for Experimental Agriculture, Stockholm, partly by Dr. Hj. von Feilitzen, Director of the Swedish Peat Society, Jönköping, Sweden. Prof. Söderbaum's earlier investigations are reported in "The Experiment Station Record," edited by the United States Department of Agriculture, Washington, vol. xiv., No. 10, 1903, pp. 951-2, and he has also summed up the result of his investigations under the title of "Vegetationsversuche mit gefälltem Calciumphosphat" in the *Zeitschrift fur das landwirtschaftliche Versuchswesen in Oesterreich*, 1908, pp. 506—10. Dr. von Filitzen has communicated the chief results of his investigations in the *Journal fur Landwirtschaft*, 1910, pp. 33—43.

As Dr. von Feilitzen is going to give an account of his further investigations at the Congress, I will here only briefly mention the chief result of his and Prof. Söderbaum's culture trials.

The result of the experiments in cultivation is that the citrate-soluble phosphoric acid in the bicalcic phosphate proves to possess the same fertilising value as the water-soluble phosphoric acid in the superphosphate, and consequently the same value as a trade product. That result might, indeed, have been foreseen, inasmuch as it is probable that the superphosphate in the soil is rapidly transformed into bicalcic phosphate through the agency of the compounds of lime present there. This result is supported by the trials carried out by practical agriculturists, who are well satisfied with both the result of the phosphate and its qualities in general. Owing to its high percentage the freight charges are low for the valuable ingredient, and a very small amount need be manipulated by the farmer. It is in all other respects easy to handle, and does not damage the sacks in the least.

The Superior Advantages of the Electrolytic Method.

The merits of the electrolytic method are as follows:—

(*a*) It admits of the use of cheap low percentage raw phosphate not available for the superphosphate nor available for the superphosphate industry.

(*b*) By it a phosphate containing 35 to 38 per cent of soluble phosphoric acid is obtained even from low percentage raw material.

(*c*) Freightage for a given quantity of phosphoric acid in the finished article is only about half that in the case of ordinary superphosphate.

(*d*) Retrogradation of soluble phosphoric acid when stored does not occur.

(*e*) The raw phosphate need not be reduced to a finely powdered state.

(*f*) Bicalcic phosphate can be employed as a fertiliser on all kinds of soil, even on sandy and boggy land.

(*g*) Bicalcic phosphate will be of excellent use in the manufacture of "complete fertilisers."

(*h*) Sacks are in no wise damaged by the product.

(*i*) The product is a finely divided white powder which s easily spread on the field.

The process is now being carried out in a small factory, the first factory belonging to the Difosfat Company, Trollhättan, Sweden.

THE SCIENTIFIC WEEK.

(*From Our Own Paris Correspondent*).

The F-rays.

The scientific world has been somewhat startled by the sensational discovery announced by the newspapers that an Italian physicist, Ulivi, had discovered the means of capturing or manufacturing artificially the infra-red rays of the solar spectrum, and of directing them at will, at a distance of more than 20 kilometres. After the discovery of so many radiations with which we are already acquainted—the X-rays, the α-rays, β-rays, γ-rays, after the Hertzian radiations which exist; and the hypothetical radiations, the N-rays of Prof. Blondlot, the N-rays of Major Darget—we have now the F-rays.

For the F-rays is the name that Ulivi has given to the infra-red rays that he has been able to produce artificially. The radiations would seem to have the property of being able to make certain explosives, such as dynamite, melinite, lyddite, pyroxylin powders, explode at a distance spontaneously, if only these diverse matters are in contact with a metallic armature.

To the west of the Havre roads in front of the sea-side place of Villiers, M. Ulivi has gone through a series of experiments before a certain number of important person ages of the French war ministry. Some submarine mines had been placed at distances of 600 metres apart over a distance of 6000 metres. M. Ulivi directed the cone of the parallel waves of his F-rays on to these different floating mines. They blew up with marvellous precision, one after the other. We have no other information concerning M. Ulivi's discovery, which, if it is confirmed, may have most formidable and unexpected applications. The fact that superior officers of the French staff and Captain Ferrie, whose numerous works on wireless telegraphy are well known, were present at these different trials, is a proof of the reality of the discovery. It is not known, however, whether it is a calorific or electric phenomenon which brings about the explosion of the cartridges, torpedoes, and fortified casemates containing the ammunitions.

Why have We been having Cold Weather last Summer and this Summer?

Meteorologists have noticed that the average temperature of last summer was more than 2° lower than the normal average of the hot summer months. In France, in England, as well as in Central and Eastern Europe the summer was very sensibly cool. It was not known whether this unexpected coolness was to be attributed to an extra important breaking-up of the Arctic ice, or to a series of winds coming from the north, though no explanation was forthcoming of this phenomenon, from a meteorological point of view.

Measures taken at the Pic du Midi, the Puy de Dôme, the Brocken, in fact everywhere in Europe, showed an unusual retrogradation of the temperature from the middle of July. In the United States, in Australia, in Africa, the same facts were remarked, so that it was proved that the phenomenon was general, and the famous law of compensation did not apply itself to the occasion.

Messrs. Abbot and Towle observed, the former in Algeria, the latter at the Observatory of Mount Wilson, that from June 12, 1912, a marked decrease in the solar radiance had taken place. The transparency of the air seemed to be slightly obscured, so that the heat received from the sun was inferior, by a fifth, to its average value for the same season.

The cause was perfectly simple; a veil of microscopic dust had spread itself over the sky and kept back from the earth a part of the heat transmitted by the sun. This dust, disseminated in the air by aërial currents, came from a terrible eruption that had taken place at the volcano of Katmai in Alaska. This eruption began on June 6, 1912, and only stopped on the morning of the 7th. The fall of volcanic dust was so great that a layer of more than 12 cm. thick was deposited on the deck of a ship that was in those parts. On the shore the thickness of the ashes was more than 30 cm. As a simple indication, it may be mentioned that the dust deposited by the eruption of Krakatoa was not, at the same distance, more than 2 cm. thick.

It is, then, highly probable that it is to the eruption of Katmai that is due to the cold summer of last year, and it is probable that the summer of 1913, which it would seem is likely to be be equally as cool, is suffering also from the ashes still floating in the atmosphere, and which are stopping a part of the calorific radiations of the sun.

The Deformation of Bodies subjected to Strain.

Lieut.-Col. Hartmann is contributing his experimental researches concerning the deformation of solid bodies subjected to strain.

Trials have been undertaken to determine the individual modification that the grains of metals undergo in the deformed regions, according to the place they occupy.

The learned artilleryman has likewise studied the mechanism by which permanent deformations produce the increasing augmentation of resistance up to a determined value of the charge, so that he has particularly tried to bring into notice molecular tensions that are brought into existence by their deformations.

In a second series of experiments Col. Hartmann has specially studied the geometrical puckering that exterior actions produce in matter. Methodical trials have been effected with metallic tubes compressed between two parallel planes, with a view of completing the first results previously obtained, thanks to a very great variety in the dimensions as well as in the preparation of the pieces experimented upon.

The cinematograph has been employed in the most interesting cases, to obtain successive images of deformation at instants very near to each other. Moreover, the study has been extended to bodies of various forms, and to diverse kinds of strain. These last researches are not yet completed; those which are at present being pursued seem likely to supply the explanation of the phenomenon of the regular distribution of the puckering; the interest of which is so much the greater since it brings into play the elastic properties of matter that are frequently observed in nature.

The Production of Carbide of Calcium.

The world's production of carbide of calcium is progressing. According to the latest statistics published by the *Journal of the Electric Kiln and the Electrolysis* it reached 300,000 tons in 1912. This progress is due, not so much to the development of the applications of acetylene as to the continually increasing extension of the manufacture of cyanide, used as a manure in agriculture.

In Europe it is Germany that holds the record for the consumption of carbide. In 1911 she imported 37,000 tons, and 48,000 in 1912; the exportations nil. Sweden is the country that manufactures the most carbide and that consumes the least. The factories of Odda are provided with the means of manufacturing 80,000 tons of carbide of calcium for the preparation of manure. In 1912 Switzerland exported 5 million francs worth of carbide. Austria-Hungary also exports nearly 11,000 tons per

annum. England, on the contrary, only imports quantities of carbide varying between 14,000 and 18,000 tons, As for France, her importations during the years 1910, 1911, 1912 were respectively 445, 2162, 3302 tons; the exportations were 4824, 5058, 6225 tons. It is especially the development of lighting by acetylene gas in the French colonies that has increased so regularly the figures of exportation.

COLOURED PHOTOGRAPHY ON TISSUES.

Messrs. Valette and Feret, of the National Gobelin Tapestry Manufactory, have recently explained to the Society of Encouragement of National Industry, a remarkable process of their invention destined to reproduce on tissues decorative effects that up till now have never been attained by any process. It is an application of trichromy to tissues. The proofs are obtained by three successive printings, blue, yellow, red, from three selected photographic clichés. The tissue is rendered sensitive by the help of diazoic sulphates mixed with alkaline phenyl products, which have the property of producing colouring matters only under the influence of light.

The indispensable adjustment for the precise superposition of the three printings is effected by means of a special frame with notches. This adjustment may be performed with great exactness, in spite of successive manipulations. The applications of this process are the same as those of printed tissues in general, but more especially for rich articles of a limited number, and which it is difficult to execute by machine, such as tapestries, hangings, fans, sachets, reproductions of pictures, and even of portraits taken from life.

NOTICES OF BOOKS.

A Text book of Rand Metallurgical Practice. By RALPH STOKES, JAS. E. THOMAS, G. O. SMART, W. R. DOWLING, H. A. WHITE, E. H. JOHNSON, W. A. CALDECOTT, A. McA. JOHNSTON, C. O. SCHMITT. Volume I. Second Edition. London: Charles Griffin and Co., Ltd. 1913.

No better proof could be adduced of the great value of this book than the fact that the first large edition of it was exhausted within twelve months of its publication, and the high opinions expressed of its merits have been fully justified. Very few changes have been made in the second edition, beyond some corrections of small errors and the amplification of some of the tables and statistics.

Chemistry. By GEORGES DARZENS. London: Constable and Co., Ltd. 1913.

THIS book is one of a series of monographs called "Thresholds of Science," which was first published in France; it is presumably a translation, although no mention of a translator is made on the title page. In the first part of it easy experiments are described, such as could be performed with simple apparatus in an ordinary room or a very meagrely equipped laboratory. These experiments are intended to illustrate the elementary principles of physical and general chemistry and the laws of chemical combination, and to give some knowledge of the properties and reactions of the more important elements and compounds. This part of the book does not differ materially from the usual type of text-book of elementary chemistry intended for beginners. The section which deals with applied chemistry gives interesting short accounts of metallurgy, the manufacture of glass, soap, perfumes, &c., and describes some rather unusual experiments which are sure to arouse the interest of the young student.

Disinfection and Disinfectants. By M. CHRISTIAN. Translated from the German by CHARLES SALTER. London: Scott, Greenwood, and Son. 1913.

MODERN methods of disinfecting are very thoroughly and systematically treated in this book, which gives an admirable account of the results which have been obtained by the scientific study of this branch of hygiene. Physical methods of disinfecting are first discussed, including treatment by dry heat, steam in various conditions (superheated, under pressure, &c.), light and other rays, electric currents, and mechanical influences. Different types of apparatus for the purpose are described and illustrated, and some methods of sterilising food, such as the pasteurisation of milk, are included. The second part of the book deals with chemical disinfection, and gives succinct directions for its practical application. The various reagents are grouped according to their chemical natures, and the strength and efficacy of many patent preparations are discussed. Different methods of disinfecting rooms without apparatus are included, and a chapter on combined methods of disinfection brings to a conclusion a thoroughly scientific account of the most recent methods of preventing the spread of diseases.

Livingstone College Year-book. Centenary Number, 1913. Livingstone College, Leyton, E.

THIS report of the work, aims, and objects of Livingstone College contains a short account of the progress made in Tropical medicine during the year 1912, and, although no very startling discoveries have been made, much valuable research work has been done, especially on sleeping sickness and the treatment of dysentery. Some important books on tropical medicine and hygiene which have recently appeared are shortly reviewed, and brief notes on new drugs and preparations which have been placed on the market are added.

CORRESPONDENCE.

SWEDISH TAR AND WOOD BY-PRODUCTS.

To the Editor of the Chemical News.

SIR,—In enclosing a copy of our Special Tar and Wood By-product Number we beg to state that any of your readers interested in the wood tar and allied trades can receive, post free, a copy of this publication by writing to us, mentioning the notice to this effect, which we trust you will kindly insert in your esteemed Journal.—I am, &c.,

LOUIS ZETTERSTEN, Secretary.
For the Swedish Chamber of Commerce in London.

Literary Intelligence.—Amongst the new scientific books to be issued in the autumn by Messrs. J. and A. Churchill are the following:—"Industrial Organic Analysis" (For the Use of Technical and Analytical Chemists and Students), by Paul S. Arup; with a Fore word by Dr. J. C. Irvine, Professor of Chemistry at the University of St. Andrews. "Quantitative Analysis in Practice" (an Introductory Course designed for Colleges and Universities), by John Waddell, Assistant Professor of Chemistry, School of Mining (Queen's University), Kingston, Canada. "Bloxam's Chemistry, Inorganic and Organic," Tenth Edition, thoroughly revised by A. G. Bloxam and Dr. S. Judd Lewis; many new illustrations are added. "Practical Chemistry" (Qualitative Exercises and Analytical Tables for Students), by the late J. Campbell Brown, Professor of Chemistry, University of Liverpool; Sixth Edition, Revised by Dr. G. D. Bengough, Lecturer on Metallurgy, University of Liverpool. "Dental Anatomy," Human and Comparative, by C. S. Tomes; Seventh Edition, Revised by Dr. Marett Tims and A. Hopewell-Smith. A radical revision has been undertaken, both as regards the text and the illustrations.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clvi., No. 23, June 9, 1913.

Reactions between Water and Sulphurous Acid at Various Temperatures. Formation of Hydrosulphurous Acid.—E. Jungfleisch and L. Brunel.—Water and sulphurous anhydride react at temperatures below 160° and even at the ordinary temperature. The reaction is slower the less concentrated the sulphurous solution is and the lower the temperature. About 160° the transformation produces sulphur and sulphuric acid, which are the ultimate terms of the reaction. Their formation takes place in two stages. In the first, hydrosulphurous and sulphuric acids are formed, and in the second stage the former splits up into sulphur and sulphuric acid. These transformations appear to be accompanied by secondary reactions.

Use of Calcium Carbonate as Catalyst for Organic Acids and Anhydrides.—Paul Sabatier and A. Mailhe.—The transformation of organic acids into acetones can readily be effected if precipitated calcium carbonate is used as catalyst, and this method of preparing propanone and diethyl ketone is very convenient. The anhydrides of the acids undergo a similar reaction.

Synthesis of Carbon Oxycyanide by Ultra-violet Rays.—Daniel Berthelot and Henry Gaudechon.—Mixtures of CO and C_2N_2 were exposed in quartz tubes to the mercury lamp light for twelve hours. After about a quarter of an hour a yellowish red deposit of carbon oxycyanide was seen on the cold part of the tube. From the change of volume which occurs it appears that the composition is CN.CO.CN. The solid oxycyanide when heated to 200° does not volatilise, but gives up small quantities of oxygen. It is soluble in alkalis. With water it undergoes the following reaction: $CN.CO.CN + HOH = CO_2 + 2HCN$.

Quantitative Separation of Iron and Chromium.—F. Bourion and A. Deshayes. Chromium oxide can be separated from iron oxide by a method based upon the insolubility in water of anhydrous chromic chloride. The mixture of oxides is subjected to the action of a slow current of chlorine containing sulphur chloride vapour, the temperature being gradually increased from 200° to 650°. This method can be recommended for mixtures which are poor in chromium, and also for mixtures of any composition, provided that the oxides have been calcined.

Constitution of Paramolybdates and Paratungstates.—H. Copaux.—Sodium molybdoaluminate is best represented by the formula $[Al(Mo_2O_7)_3]Na_3 + Aq$, which is derived from the orthoaluminate, AlO_3N_3, by the substitution of three divalent radicals, Mo_2O_7, for three atoms of oxygen. Molybdic anhydride, MoO_3, corresponds to an orthomolybdic acid, MoO_6H_6, the salts of which are unknown in the free state, but become stable by the introduction of Mo_2O_7 radicals. If three oxygen atoms are thus replaced the formula $\left[\begin{matrix}Mo.(Mo_2O_7)_3\\ O_3\end{matrix}\right]M_6+Aq$ is obtained (M being a monovalent metal). This represents the paramolybdates, which are substituted orthomolybdates in which the molybdenum plays two parts, that of generator of acid and substituent. The paratungstates the author represents by the formula $[H(Wo_2O_7)_3]M_5 + Aq$. The study of the absorption of light and the dehydration under the action of heat confirms these formulæ.

Derivatives of β-Methylcyclopentanone.—Marcel Godchot and Félix Taboury.—When dry chlorine acts on β-methylcyclopentanone in diffused light at a temperature not exceeding 25°, β-methyl-α-chlorocyclopentanone is formed. This is hydrolysed by water, giving a methylcyclopentanolone, which on oxidation yields α-methylglutaric acid. β-Methylcyclopentenone is also formed by the hydrolysis of the chloro compound.

Preparation of Diglyceric Alcohol.—Jean Nivière.—To prepare diglyceric alcohol equimolecular proportions of glycide and glycerin are heated on the water-bath for six or seven hours. The mixture is then acetylated by boiling with acetic anhydride, and the tetraacetine which is obtained between 195—205° under 1 to 2 mm. pressure, is saponified with alcoholic soda. The alcohol is a yellowish very viscous liquid, which is insoluble in ether, soluble in water and alcohol, and hygroscopic like glycerin.

Vol. clvi., No. 24, June 16, 1913.

Ketimines.—Charles Moureu and Georges Mignonac.—Ketonic imines which contain the divalent reside =NH may be called ketimines. To prepare diphenylketimine, $C_6H_5{-}\underset{\displaystyle NH}{\underset{\|}{C}}{-}C_6H_5$, a compound is first made of benzonitrile and phenyl magnesium bromide. It is washed with ether and mixed with ammonium chloride. Decomposition occurs, and all the magnesia dissolves. The whole is then shaken with ether, and the ethereal liquid is dried over anhydrous sodium sulphate and saturated with dry hydrochloric acid gas. The ketimine is thus precipitated as hydrochloride. This is a general method of preparing ketimines in which the residues attached to the functional group are aromatic; it can also be applied to the case of the mixed fatty aromatic ketimines, which, however, are more easily decomposed by water. The ketimines are usually oils or solids of low melting-points. They are basic substances giving crystalline salts, and are unsaturated. The ketimine function appears to be very active, and takes part in many reactions.

Bromination of Secondary Hydroaromatic Ketones and Alcohols.—F. Bodroux and F. Taboury.—The authors have already shown that the bromination of cyclohexanone and cyclohexanol in carbon tetrachloride solution gives the same compound, a tetrabromocyclohexanone. The same process applied to some homologues of this ketone and alcohol gives similar results, a tri- or tetrabrom derivative being obtained. These derivatives are not very stable, and at a temperature a little above their melting-point they decompose into bromine, hydrobromic acid, and brominated phenol. The same transformation occurs slowly under the influence of light at the ordinary temperature.

Quantitative Study of Absorption of Ultra-violet Rays.—Jean Bielecki and Victor Henri.—The authors have investigated the absorption of the ultra-violet rays upon the following substances:—Primary, secondary, tertiary amines, diamines, nitriles, carbylamines, amides, ketoximes, and aldoximes. They find that the value of ε increases regularly as λ diminishes, down to 2144. The absorption by the amines increases with the number of carbon atoms contained in them. When the hydrogen atoms of ammonia are replaced by radicles C_nH_{2n+1} the absorption increases very rapidly. Substances containing a nitrogen with a triple bond or those in which nitrogen is pentavalent absorb very little. The amides behave like the corresponding acids, thus the substitution of the NH_2 group increases the absorption, and the absorption by the oximes is less marked than that of the amines.

Bulletin de la Société Chimique de France. Vol. xiii.-xiv., No. 12, 1913.

Catalytic Hydrogenation of Methylcyclopentanones.—Marcel Godchot and Félix Taboury.—β-Methylcyclopentanone when subjected to the action of hydrogen at 150° in presence of reduced nickel gives a liquid which can be separated into two fractions by distillation. The first, which comes over between 140° and 150°, consists chiefly of β-methylcyclopentanol, while the second portion, distilling between 244° and 246°, consists of the ketone ββ-dimethylcyclopentylcyclopentanone. The reaction in the case of α-methylcyclopentanone is analogous, the chief product being again the double ketone.

THE CHEMICAL NEWS.
VOL. CVIII., No. 2806.
(STUDENTS' NUMBER).

UNIVERSITIES AND COLLEGES.

UNIVERSITY OF LONDON.

CANDIDATES for any Degree in this University must either have passed the Matriculation Examination in this University, or be admitted under the Statute which provides that the Senate may admit graduates of or persons who have passed the examinations required for a degree in other Universities approved by it. This and all other Examinations of the University, together with the Prizes, Exhibitions, Scholarships, &c., are open to Women upon exactly the same conditions as to Men.

There are three Examinations for Matriculation in each year; commencing on the second Monday in September, January, and June (or July, as may hereafter be determined).

Every Candidate for the Matriculation Examination must apply to the Principal for a Form of Entry on or before August 20, which must be returned fourteen days before the commencement of the September Examination; or must apply for a Form of Entry on or before November 25, which must be returned on or before December 1, for the January Examination; or must apply for a Form of Entry on or before April 25, which must be returned on or before May 1, for the June (or July) Examination; accompanied in each case by the proper Fee, and by a Certificate showing that the Candidate will have completed his Sixteenth Year on or before January 14 for the January Examination, July 31, the end of the Secondary School Year, for the June Examination, and September 15 for the September Examination.

Every candidate entering for the Matriculation Examination must pay a Fee of £2.

Intending Students (Internal and External) should obtain the "Regulations and Courses" from the Registrar, University of London, South Kensington, S.W.

Several valuable Scholarships and Exhibitions are available to students.

UNIVERSITY OF OXFORD.

Waynflete Professor of Chemistry—W. H. Perkin, M.A., F.R.S.

Lees Reader in Chemistry—(Vacant).

Every Student must reside in one or other of the Colleges or Halls, or in licensed lodgings, for a period of three years. Students of Chemistry can obtain the degree of B.A. by passing preliminary examinations in Arts and in Science, and a final Honour examination in Chemistry. Chemistry may also be taken as part of the examination for a Pass degree. Graduates of other Universities and other persons suitably qualified can obtain the degree of Bachelor of Science after an approved course of study or research and two years' residence.

University Laboratory.—Demonstrators, W. W. Fisher, M.A., J. E. Marsh, M.A., F.R.S., N. V. Sidgwick, M.A., A. F. Walden, M.A., B. Lambert, M.A., F. D. Chattaway, M.A., D.Sc.—The fee for students working in the Laboratory for three days in the week during the Term is £3; for students working every day, £5.

There are also laboratories which specialise in different parts of the subject:—*Physical Chemistry*, Balliol and Trinity College Laboratory: D. H. Nagel, M.A., H. B. Hartley, M.A. *Inorganic Chemistry*, Christ Church Laboratory: A. Angel, M.A. *Quantitative Analysis*, Magdalen College Laboratory: J. J. Manley, M.A. Jesus College Laboratory: D. L. Chapman, M.A. Queen's College Laboratory: Rev. G. B. Cronshaw, M.A.

Scholarships of about the value of £80 are obtainable at the majority of the colleges, by competitive examination in Natural Science.

More detailed information may be obtained from the Examination Statutes; the Student's Handbook to the University; and from the professors and college tutors.

UNIVERSITY OF CAMBRIDGE.

Professor of Chemistry—William J. Pope, M.A., F.R.S.

Jacksonian Professor of Natural and Experimental Philosophy—Sir James Dewar, M.A., F.R.S.

Goldsmiths Reader in Metallurgy—Charles T. Heycock, M.A., F.R.S.

The Student must enter at one of the Colleges or Hostels, or as a Non-collegiate Student, and keep terms for three years by residence in the University. He must pass the previous examination in Classics and Mathematics, which may be done in any term of residence or before commencing residence. He may then proceed to take a Degree in Arts, either continuing mathematical and classical study, and passing the ordinary examinations for B.A., or going out in one of the Honour Triposes.

A graduate of another University may be admitted as an "advanced" student, and obtain a degree after two years' residence in the University, either by examination or by presentation of a thesis describing original research.

Facilities for research work are provided both in the Chemical Laboratories and in the Metallurgical Laboratories.

The scholarships, ranging in value from £20 to £100 a year, are chiefly given for mathematical and classical proficiency. Scholarships, or Exhibitions, are given for Natural Science at the several Colleges; the dates of the examinations vary, but are always fully advertised.

The Chemical Laboratories of the University are open daily for the use of the Students. The Demonstrators attend daily to give instruction. A list of the lectures and practical courses is published annually, in June, in a special number of the *Cambridge University Reporter*, which may be had from the Cambridge Warehouse, in Paternoster Row, or through any bookseller.

Non-collegiate Students are allowed to attend certain of the College Lectures and all the Professors' Lectures, and have the same University status and privileges as the other Students. Full particulars may be obtained by forwarding a stamped directed envelope to the Assistant Registrary, Cambridge, from the *Cambridge University Calendar*, or from the "Students' Handbook to Cambridge."

UNIVERSITY OF DUBLIN.
TRINITY COLLEGE.

Professor of Chemistry—Sydney Young, D.Sc., F.R.S.

Professor of Applied Chemistry—Emil A. Werner, F.C.S., F.I.C.

Demonstrator—W. C. Ramsden, F.C.S.

Junior Demonstrator—H. Krall, B.A.

The general Quantitative and Research Laboratories include working accommodation for about 130 Students. The Laboratories will open on October 1st. Lectures will commence on November 4th.

The Laboratories and the Lectures of the Professor of Chemistry can be attended by Students who do not desire to reside in the University or proceed to its Degrees.

The full Course of General and Analytical Chemistry occupies three years, but a Student is free in his third year to devote most of his time to a special department of Pure or Technical Chemistry. Students can enter for any portion of the Course. The Lectures delivered are:—

1. *Inorganic Chemistry and Chemical Philosophy*.—Elementary, first year; Advanced Inorganic Chemistry, second year; Physical Chemistry, third year.
2. *Organic Chemistry*.—General, second year; advanced, third year.
3. *Metallurgy*.—A Course for Engineering and Technical Students.
4. *Agricultural Chemistry*.—Theoretical and Practical Courses.

The Laboratories are open every day from 10 to 5 o'clock (except Saturdays, when they close at 1 o'clock).

The Summer Course of Practical Chemistry for Medical Students begins early in April and terminates about the end of June.

A special course for Dental Students will be given.

The University of Dublin grants the Degree of Doctor of Science to graduates of Master's standing whose independent researches in any branch of Science are of sufficient merit.

By recent decrees, Prizes in Chemistry and Physics will be given in future at the October (Arts) Entrance Examination, and also at the Terminal Examinations of the Junior and Senior Freshmen Years.

Similarly, two Science Scholarships will be obtainable by Undergraduates, and tenable for five years. The Foundation Scholars receive £20 per annum, they have free commons, and their chambers for half the charge paid by other students; their tutorial fees are at one-fourth the usual rates.

KING'S COLLEGE.
(University of London).

Senior Professor of Chemistry—J. M. Thomson, LL.D., F.R.S.

Professors — Herbert Jackson, F.C.S., and P. H. Kirkaldy, F.C.S.

Lecturer and Demonstrators—S. W. Collins, B.Sc., L. E. Hinkel, B.Sc., Thomas Wright, B.Sc., and E. W. Skelton, B.Sc.

The Academical Year consists of Three terms. The days fixed for the commencement of Terms in 1913-1914 are Oct. 1, Jan. 14, and April 29.

Students of the First Year are admitted to the Course of Theoretical and Applied Chemistry. The Course commences with a view of the conditions suitable for the production of Chemical Phenomena, after which the laws of Chemical Attraction are discussed, and the Non-metallic Elements and their principal compounds are described. The Metals and their principal compounds are next examined, care being taken to point out the applications of the Science to the Arts. Examinations of the Class, both *vivâ voce* and by written papers, are held at intervals during the course at the usual Lecture hour.

Second Year.—Students attend in the Laboratory twice a week, and they go through a course of Chemical Analysis and Elementary Volumetric Analysis.

Experimental and Analytical Chemistry in the Laboratory.—The object of this Class is to afford to Students who are desirous of acquiring a knowledge of analysis, or of prosecuting original research, an opportunity of doing so under the superintendence of the Professor and Demonstrator; Students may enter, upon payment of extra fees, at any time except during the vacation, and for a period of one, three, six, or nine months, as may best suit their convenience. The laboratory hours are from ten till five daily, except Saturday.

In addition to the Laboratory Fee, each Student defrays the expenses of his own experiments. The amount of this expense, which is comparatively trifling, is entirely under his own control.

For fuller details the separate Syllabuses provided for each class should be consulted.

UNIVERSITY COLLEGE.
(University of London).

Professors—J. Norman Collie, Ph.D., F.R.S. (Organic Chemistry); F. G. Donnan, M.A., F.R.S. (Inorganic and Physical Chemistry).

Assistants—R. W. Gray, Ph.D.; S. Smiles, D.Sc.; Katharine A. Burke, B.Sc.; R. E. Slade, D.Sc.; W. B. Tuck, D.Sc.; Irvine Masson, M.Sc.

The Session is divided into three Terms, as follows:—First Term, from September 30 to December 19; Second Term, from January 13 to March 27; Third Term, from April 28 to June 15.

Introductory Course of Inorganic Chemistry.

Tuesday and Thursday, at 11. Practical, Thursday, 2 to 3.30, or 3.30 to 5. Fee, £10 10s.

The principles of Elementary Inorganic Chemistry, illustrated chiefly by reference to:—Air, water, salt, ores, fuels, coal industry, furnace products, soda industry, mortar, cement, glass making, nitre and nitrogen-fixation; and other technical processes.

Junior Course of Inorganic Chemistry.

The more important inorganic substance will be dealt with. Special attention will be paid to general points of view, and to the application of physico chemical laws and methods.

First and Second Terms: The Class meets three times a week, on Mondays, Wednesdays, and Fridays, at 9, for Lectures, Examinations, and Exercises.

Third Term: Lectures will be given on Mondays and Fridays at 9 and another hour to be arranged.

Fees: Course, £7 7s.; First or Second Terms, £4 4s.

A Practical Class will meet throughout the Session.

Courses of Physical Chemistry.

October to February: Tuesday and Thursday at 9.
February to July: Tuesday and Thursday at 9.

The Courses comprise Stoichometry, the Liquid and Solid States of Matter, the Phase Rule, Thermochemistry, and in general the Application of Physical Methods to the Solution of Chemical Problems, Chemical Statics, the Electrolytic Dissociation Theory, Chemical Dynamics, and Chemical Thermodynamics.

Fees:—Courses, £5 5s.; Term, £2 2s.

Senior Course of Inorganic Chemistry.

This Course will begin about the middle of February; Tuesday and Thursday at 9. Fee, £3 3s.

Organic Chemistry.

Mon. at 12, Wed. and Fri. at 9, during the session.

This Course is suitable for Students who intend to study Chemistry from a scientific standpoint. No previous knowledge of Organic Chemistry is expected of those attending the Class, which should, however, be taken concurrently with the Course of Physical Chemistry, and with Practical Organic Chemistry in the Laboratory.

Fee:—For the Course, £6 6s.; for a Term, £2 12s. 6d.

An Advanced Course will be held twice a week throughout the Session for those engaged in prosecuting research in Organic Chemistry. Fee, £5 5s.; Term, £2 2s.

Practical Classes.

Practical Classes in Inorganic and Organic Chemistry are conducted by the Assistants.

Laboratories of General and of Organic Chemistry.

The Laboratories are open daily from 9 a.m. to 5 p.m., Saturdays excepted, from October until the middle of July, with a short recess at Christmas and at Easter.

Fees: for the Session, £26 5s.; six months, £18 18s.; three months, £10 10s.; one month, £4 4s.

Three specified days a week:—for the Session, £15 15s.; six months, £11 11s.; three months, £6 6s.; one month, £2 12s. 6d., exclusive of expense of materials. Students may enter at any period of the Session.

When accompanied by, or preceded by, attendance on the Lectures on Inorganic and Organic Chemistry, the Laboratory Courses qualify Students in the application of Chemistry to Manufactures, Metallurgy, Medicine, or Agriculture, &c.

There is also a Chemical Library containing the chief Journals and Standard Works on Chemistry.

Certificates of Honour are granted to competent Students on the work done during the Session. Several valuable Scholarships are available to students.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY.

Emeritus Professors—Sir W. A. Tilden, D.Sc., F.R.S., and Sir T. E. Thorpe, C.B., F.R.S., &c.

Professor and Director of the Chemical Laboratories.—H. Brereton Baker, D.Sc., F.R.S., &c.

Professor of Chemical Technology and Fuel Chemistry—W. A. Bone, F.R.S.

Assistant Professors—M. O. Forster, Ph.D., D.Sc., F.R.S.; J. C. Philip, M.A., Ph.D., B.Sc.; B. Mouat Jones, M.A.

The Imperial College of Science and Technology, incorporated under the Royal Charter of July 8, 1907, is an institution or group of associated colleges with its principal seat at South Kensington.

The purposes of the Imperial College are to give the highest specialised instruction, and to provide the fullest equipment for the most advanced training and research in various branches of science, especially in its application to industry; and to do all and any of such things as the Governing Body consider conducive or incidental thereto, having regard to the provision for those purposes which already exists elsewhere.

For these purposes, the Governing Body, subject to the provisions of the Charter, are to carry on the work of the Royal College of Science, and the Royal School of Mines, and may establish Colleges and other Institutions or Departments of Instruction. Any Institution or Department so established, and, subject to the conditions of the Charter, the Central Technical College of the City and Guilds of London Institute, are to be integral parts of the Imperial College; and the Central Technical College is to be called and known in future as the City and Guilds College.

The Charter further provides that the Imperial College shall be established in the first instance as a School of the University of London. Students of the Imperial College who have matriculated at the University of London may therefore proceed to the Science degree of the University as "Internal Students."

Attention is particularly directed to the conditions of admission and to the extended facilities for Research Work.

The ordinary courses of instruction are planned so as to extend over four years, and are generally similar for all divisions during the first year, and to a less extent during the second year, after which they are specialised according to the particular course which the student is taking.

The following Diplomas have been awarded in the past to Students of the several constituent Colleges:—

The Associateship of the Royal College of Science (A.R.C.S.) in one or more of the following divisions:—Mechanics, Physics, Chemistry, Botany, Zoology, Geology.

The Associateship of the Royal School of Mines (A.R.S.M.) in one or more of the following divisions:—Metallurgy, Mining.

The Associateship of the City and Guilds Institute (A.C.G.I.) will be awarded in Engineering (Civil and Mechanical), Engineering (Electrical).

Twelve entrance scholarships are given in September each year, and post graduate scholarships are available for enabling fourth and fifth year students to complete their courses. Three Research Fellowships, founded by Mr. Otto Beit, of £150 a year, tenable at the Imperial College, are offered annually to post graduate students of this College, as well as to graduates of Universities in the United Kingdom.

Full details can be obtained from the College Calendar, published by Eyre and Spottiswoode (or through any bookseller), price 6d.

THE SCHOOL OF PHARMACY OF THE PHARMACEUTICAL SOCIETY OF GREAT BRITAIN.

The 72nd Session will commence on Oct. 1, 1913.

Professors—Chemistry, Arthur W. Crossley, D.Sc., Ph.D., F.I.C., F.R.S.; Pharmaceutics, Henry G. Greenish, F.I.C., F.L.S. (Dean).

A Course of Lectures on Physical, Inorganic, and Elementary Organic Chemistry commences in October and terminates at the end of June. An Advanced Course of Lectures begins in October and extends to the end of March. These Lectures are adapted to the requirements of Pharmaceutical and Medical Students, and also of those who are proceeding to degrees at the University of London, or who are preparing for the examinations of the Institute of Chemistry.

Entries may be made for single classes. Certificates of attendance at the two Courses of Lectures on Chemistry and at the Chemical Laboratories are accepted as evidence of chemical training by the Institute of Chemistry in connection with the Examinations for the Associateship, and also by the Conjoint Board of the Royal Colleges of Physicians and Surgeons, as well as by other examining bodies. Certificates of attendance at the Course of Pharmacy is also accepted by the Conjoint Board.

Prospectuses and further information may be obtained from the Dean of the School, 17, Bloomsbury Square, London, W.C.

UNIVERSITY COLLEGE OF WALES, ABERYSTWYTH.

UNIVERSITY OF WALES.

Professor—A. Findlay, M.A., D.Sc. (Aberdeen), Ph.D. (Leipzig), F.I.C.

Lecturer and Demonstrator—T. Campbell James, M.A., Trinity College, Cambridge, D.Sc. (Wales).

Assistant Lecturer and Demonstrator—A. Brooke, Ph.D. (Strassburg).

Lecture Assistant—W. Beynon Williams, B.Sc.

Student Assistant—William Thomas, B.Sc. (Wales).

Lecturer in Agricultural Chemistry—J. Jones Griffith, B.Sc. (Wales).

The College is open to men and women students above the age of sixteen years. The Session commences on Oct. 1st, on which day all Students will be expected to meet the Professors in the Examination Hall of the College.

Lecture Courses.—(1) Intermediate Science Course; four lectures weekly throughout the Session. (2 and 3) B.Sc. Courses; A, three lectures weekly on Organic Chemistry; B, three lectures weekly on General and Physical Chemistry. (Courses A and B will generally be given in alternate Sessions; for 1913-1914, Course A). (4 and 5) Courses in Agricultural Chemistry. For students in their first year, 3 lectures, and for those in their 2nd year, 2 lectures weekly during the Michaelmas and Lent terms.

Laboratory Courses.—The Laboratories are open daily from 9 a.m. to 1 p.m. and from 2 to 6 p.m., Saturdays 9 a.m. to 1 p.m. Regular Courses of practical work, suitable for the B.Sc. degree of the Universities of London and Wales, or for the Associateship of the Institute of Chemistry, can be followed. Facilities are given for Students wishing to undertake research work. Special Courses will be arranged for those who intend to follow Medicine or Pharmacy, or any one particular branch of Applied Chemistry, always provided that such Students possess the requisite knowledge of Theoretical Chemistry. The hours will be arranged, as far as possible, to suit the requirements of the individual Student.

The College is recognised by the University of Edinburgh and the Royal University of Ireland, and by the Colleges of Physicians and Surgeons of England, Scotland, and Ireland as an institution at which the instruction necessary for their respective Diplomas in Medicine, in Chemistry, Physics, and Biology may be given. One year for graduation in Medicine and two years for graduation in Science may be spent at Aberystwyth.

Fees.—The Fee for the whole Session, if paid in advance, is £17. This composition fee enables the Student to attend any or all the Classes and Laboratories of the College.

Scholarships and Exhibitions varying in value from £10 to £40 per annum will be offered for competition at examinations which commence on September 16, and exhibitions are awarded at the end of the Session on the results of the class examinations.

Intending Students requiring further information are recommended to write to the Registrar for a copy either of the General Prospectus or of one of the Special Pros-

pectuses issued for the Agricultural and Normal Departments.

UNIVERSITY COLLEGE OF NORTH WALES, BANGOR.

A Constituent College of the University of Wales.

Chemistry.—Professor, K. J. P. Orton, M.A., Ph.D., F.I.C. Assistant Lecturers and Demonstrators, Alice E. Smith, D.Sc., J. O. Hughes, B.Sc. Lecturer in Agricultural Chemistry, H. E. Jones, B.A., B.Sc.

Physics.—Professor, E. Taylor Jones, D.Sc. Assistant Lecturers and Demonstrators, A. H. Ferguson, B.Sc., and W. E. Williams, B.Sc.

The Session opens September 30th, 1913. All regular classes are open to men and women students above the age of 16 years. The following Courses of Lectures will be given.

Intermediate Course.—Inorganic Chemistry and Elementary Physical Chemistry. Fee for the Session, £5.

B.Sc. Course.—Organic Chemistry. Fee for the Session, £3 15s. Advanced Lectures on Organic Chemistry, £1 5s.

Agricultural Chemistry.—Fee, £2 10s.

Laboratory Courses.—The laboratory is open on five days of the week from 10 a.m. to 5 p.m. for instruction in Chemical operations and in the Application of Chemistry to Medicine and the Industrial Arts. Fees: six hours per week, £1 1s. per Term; twelve hours, £2 2s.; eighteen hours, £3 3s. Composition Fee for all Laboratory Classes of the Science Degree Course taken in one year, £4 4s.

The College Courses are arranged with reference to the Degree Courses of the University of Wales (of which the College is one of the Constitutent Colleges). The Courses in Science are also suited to the requirements of Students preparing for the Science Degree Course of the University of London.

The Chemistry, Botany, Zoology, and Physics Courses are recognised for Medical graduation in the Universities of Edinburgh and Glasgow, and by the Conjoint Boards of the Royal Colleges of Surgeons and Physicians, and students can make one *Annus medicus* at the college. Students are prepared for the First Examination of the Universities mentioned, the First Examination for Medical Degrees of the University of London, and of Conjoint Board of the Royal Colleges of Surgeons and Physicians. The Science Courses are recognised for part of the science degree course of the University of Edinburgh.

UNIVERSITY COLLEGE OF SOUTH WALES AND MONMOUTHSHIRE, CARDIFF.

Professor—C. M. Thompson, M.A., D.Sc., F.C.S.

Assistant Professor—E. P. Perman, D.Sc., F.C.S.

Lecturer to Medical Students and Demonstrator—R. D. Abell, D.Sc., Ph.D., F.I.C., F.C.S.

Professor in Metallurgy—A. A. Read, M.Met., F.I.C., F.C.S.

The Session commences October 7th, and terminates on June 26th, and is divided into three terms.

The Junior Course (delivered during the Michaelmas term only) consists of about 30 lectures, and will cover the subjects prescribed for the Matriculation examinations of the University of Wales and the University of London. Fee, £2 2s.

The Intermediate Course consists of about 80 lectures; together with laboratory practice it forms the qualifying course for the Intermediate Examination of the University of Wales, and will cover the subjects required for the Intermediate Examination in Science (Part I.) of the University of London. Fee, £4 4s.

The Senior Course consists of about 80 lectures on Organic Chemistry; Fee, £3 3s.

A course on Inorganic Chemistry will be given in the Session 1914—1915.

The following lectures on Metallurgy will be given by Prof. Read:—10 lectures on Fuel; Fee, 10s. 6d. 20 lectures on General Metallurgy; Fee, £1 1s. 30 lectures on the Manufacture of Iron and Steel; Fee, £1 1s. A practical course on Iron and Steel Analysis will also be held. Practical instruction in Dry Assaying will be given in the Metallurgical Laboratory, which is fitted with the necessary furnaces and apparatus.

In the laboratory each student works independently, so that the course of study may be adapted to the requirements of the individual. Hours, 9 to 1 and 2 to 5; Saturday, 9 to 1. Fees—Six hours per week, £2 2s. per term; twelve hours, £3 3s. per term; eighteen or more hours, £4 4s. per term.

Registered medical students can prepare for the Intermediate M.B. Examination of the University of London, and spend three out of their five years of medical study in Cardiff. Medical students preparing for a Conjoint Board Surgical and Medical Diploma, or for the Diploma of the Society of Apothecaries, can spend two years in Cardiff. For further information see the prospectus of the Faculty of Medicine, which may be obtained from the Registrar.

The College is recognised as an institution at which two years of the course for the degree of Bachelor of Science of the University of Edinburgh may be spent.

Students by making a payment of £10 at the commencement of each session may compound for all lecture fees for the whole session. Laboratory fees are not included in the composition fee, but Students preparing for the Science Examinations of the University of Wales and of the University of London may, by making a payment of £13 13s. at the commencement of each Session, compound for both Lecture and Laboratory Fees during the Session.

At the entrance examination in April, and the annual examination in June, several scholarships and exhibitions are awarded. Great importance is attached to special excellence in one subject.

The College Prospectus, and also further information as to scholarships, may be obtained from the Registrar.

A Hall of Residence for Women Students is attached to the College.

UNIVERSITY OF BRISTOL.

Department of Chemistry.

Alfred Capper Pass Professor of Chemistry—Francis Francis, D.Sc., Ph.D., F.I.C.

Lecturers—O. C. M. Davis, B.Sc., D.Sc., F.I.C.; F. W. Rixon, M.Sc., PhD.

Lecturer in Inorganic and Physical Chemistry—James W. McBain, M.A., Ph.D.

Lecturer in Bio-chemistry—Max. Nierenstein, Ph.D.

Lecturer in Hygienic Chemistry—Edward Russell, B.Sc., F.I.C.

Lecture Assistant—J. H. Sturgess.

The session commences on October 1.

The Department of Chemistry is situated in the new wing of the University Buildings in Tyndall's Park, and was opened on October 1, 1910. The Department provides accommodation for 200 students, and laboratories for work in specialised branches of Chemistry have been designed and equipped with apparatus of the most modern type. All the laboratories are supplied with electric wiring for experimental purposes, and currents of any desired voltage up to 250 volts at 50 ampères from dynamo or storage cells may be obtained throughout the Department. Higher voltages and currents are available in special laboratories, for Physical Chemistry and Electro-metallurgy. Special facilities are afforded to those who desire to carry out research or to study Chemistry as applied to the different processes employed in the arts and manufactures; and a laboratory for Bio-chemistry has been specially designed for the investigations of problems on Biological lines.

Day Lectures.

General Courses.—1. General Inorganic Chemistry—Three lectures per week during Session and Laboratory work. 2. General Organic Chemistry—Three Lectures per week during one Session and Laboratory work.

3. Physical Chemistry—Two Lectures per week for two Sessions and Laboratory work.

The Laboratories are open daily from 9.30 to 5 except on Saturdays, when they are open for Senior Students only.

Courses for Graduation.—Intermediate Science—Course 1 and one day Laboratory per week. *Pass Degree*—Course 2 and 3, and at least one day Laboratory per week during two Sessions. The Chemical Society must be attended during the second and third years, and one or more of the Special Courses arranged for Honours Students. *Honours Degree*—During the first year in the Honours School Courses 2 and 3, and the second and third, Course 3, and one or more of the following Special Courses as directed, *e.g.*:—Organic Chemistry, Physical Chemistry, Mathematical Chemistry, Advanced Inorganic Chemistry, Applied Electro-chemistry, some part of Bio-chemistry.

The meetings of the Chemical Society must be attended during each Session.

Colloquium.—A weekly Colloquium will be held by members of the Staff to discuss recent advances in the various developments of Chemistry. Honours Students attend, and others interested are invited to do so.

Extract from Regulations as Regards Fees.

1. Registration Fee 7s. for a single Course; £1 1s. shall cover a perpetual registration for any number of Courses.

2. Inclusive Fee for an entire curriculum for degree of B.Sc., whether "Pass" or "Honours," shall be £21 a year.

3. The Fees for separate Courses of Lecturers in Faculty of Science shall be at the rate of £1 1s. per term, or £2 2s. a year for each hour per week for which the Course in question is offered.

The Fees for separate Laboratory practice and instruction in the Faculty of Science shall be at the rate of £2 2s. per term for each day in the week for which admission in the Laboratories is sought, with a minimum of £3 3s. in each particular case.

EVENING LECTURES.

The Laboratories are opened, for students who have attained the standard of an Inter. B.Sc. examination, from 6.30 to 9.30 p.m. on Tuesday during the Autumn and Spring Terms. Course 1 will be given on Wednesday at 8 to 9, and Course 2 or 3 on Friday at 8 to 9 p.m. during these Terms. The Lectures and Laboratory work in Course 1 will be similar to that given to Second year Students in the Faculty of Science, and that given in Course 2 or 3 to one of those given to Students studying for the Final Degrees in that Faculty.

Extract from Regulations as Regards Fees for Evening Students.

1. For Evening Students who enter on a curriculum for a Degree the Registration Fee shall be 5s., for a curriculum for a Certificate, unless the Student has matriculated, the fee shall be 10s. 6d.

2. Unless in any case otherwise prescribed, the Fees for Evening Classes in the Faculties of Arts and Science shall be 10s. 6d. for two terms, or for one term's attendance.

All communications to the University to be addressed to the Registrar. Information concerning Courses or Laboratory work in the Department of Chemistry may be obtained from the Professor.

The department of experimental physics includes various courses of lectures arranged progressively, and practical instruction is given in the physical and electrical laboratories. The Department of Engineering is designed to afford a thorough scientific education to students intending to become engineers, or to enter any of the allied professions, and to supplement the ordinary professional training by systematic technical teaching. This department includes courses specially arranged for students intending to become civil, mechanical, electrical, mining, or motor car engineers, surveyors, or architects. Those who attend the mechanical engineering course enter engineering works during the six summer months, and, in accordance with this scheme, various manufacturing engineers in the neighbourhood have consented to receive students of the University into their offices and workshops as articled pupils at reduced terms. Medical education is provided by the Faculty of Medicine of the University. Several Scholarships are tenable at the University.

MERCHANT VENTURERS' TECHNICAL COLLEGE, BRISTOL.

CHEMISTRY.

Professor—J. Wertheimer, D.Sc., B.A., F.I.C., F.C.S.
Lecturers—H. A. M. Borland, A.R.C.S.; E. E. Elt, B.Sc.
Demonstrators—E. G. Moody and H. Orr.
Assistant in Chemical Laboratory—R. K. Lloyd.

In consequence of the foundation of the University of Bristol, the College now restricts its work to Applied Chemistry in the daytime; Pure Chemistry is taught at the University College. The Engineering work of the University College has, on the other hand, been transferred to this College.

The College Evening Classes commence on Monday, Sept. 22nd.

Further detailed information may be obtained from the College Calendar, price 6d., or the Prospectus for Day or Evening Classes (1d. each).

UNIVERSITY OF BIRMINGHAM.

Professor—Percy F. Frankland, Ph.D., M.Sc., LL.D., F.R.S., F.I.C.

Assistant Lecturers and Demonstrators — Hamilton McCombie, M.A., Ph.D., B.Sc., A.R.C.S., A.I.C.; C. K. Tinkler, D.Sc.; J. E. Coates, M.Sc.; E. P. Frankland, Ph.D., B.A., M.Sc.; Ernest Vanstone, M.Sc.

Professor of Metallurgy—Thomas Turner, M.Sc., A.R.S.M.

The Session will be opened on October 7th, 1913.

The Chemical Department is housed in the new University buildings at Bournbrook.

Lecture Courses.

First Year.—A. This part of the course is arranged (1) to give a full exposition of the general principles of Chemical Science, (2) for the systematic study of the properties of the more important elements and their compounds, and (3) to indicate the chief applications of Chemistry in the Arts and Manufactures. Three hours weekly during the Winter and Spring terms. Mondays, Wednesdays, and Thursdays at 9.30 a.m. Fee, £4 4s. B. This part of the course includes an introduction to the study of Organic Chemistry, with a description of the properties, relations, and methods of preparation of the more important groups of Carbon Compounds. Three hours weekly during the Summer term. Mondays, Wednesdays, and Fridays, at 9.30 to 10.30 a.m. Fee, £1 11s. 6d.

Second Year.—Advanced Organic Chemistry.—This course extends over two years, and is divided into two parts:—(*a*) Carbon Compounds of the Fatty Series; (*b*) Aromatic and other Cyclic Compounds. Only one of these parts will be taken in each year. The class meets twice weekly by arrangement during the Winter and Spring terms. Fee, £2 2s. *Advanced Inorganic Chemistry.*—This course is devoted to the consideration of special branches of Inorganic Chemistry, and direction is also given as to the private reading which should be pursued by students. The class meets by arrangement once weekly during the Session. Fee, £1 1s.

Third Year.—A further Course in Advanced Organic Chemistry will deal with one of the above parts of the Course. The class meets two hours weekly by arrangement during the Winter and Spring terms. Fee, £2 2s. A Course on Physical Chemistry. Fee, £2 2s.

Fourth Year.—For students preparing for the B.Sc. degree with Honours in Chemistry.

Special Courses in General, Organic, and Physical Chemistry.

Practical Chemistry.

The instruction in Practical Chemistry extends over four years in the case of the Honours Degree. The Laboratory will be open daily from 9.30 to 5, except Saturdays, when it closes at 1 p.m. Fees—

	All day.	Three hours per day.	Threehours per day; five days a week.	Three hours per day; three days a week.
	Guineas.	Guineas.	Guineas.	Guineas.
One Term ..	7	4½	4	2½
Two Terms .	13	8½	7½	5
Three Terms	18	12	11	6½

A Course of short demonstrations and exercises is given by the Professor or one of his Assistants once a week. All first-year Students are required to attend, unless exempted for special reasons by the Professor. No Fee.

Special facilities are given to Advanced Students for the prosecution of original research.

Metallurgy.

There is a separate University department for Metallurgical students in which provision is made for instruction in assaying, &c.

Scholarships.

Priestley Scholarships.—Three Open Scholarships in Chemistry of the value of about £96 each are awarded annually in June.

Ascough Scholarship.—One Open Scholarship of the value of about £30 is awarded annually in July.

Bowen Scholarship.—One Open Scholarship in Metallurgy, value about £96, is awarded annually in June.

For particulars apply to the Registrar.

Excursions.

During previous Sessions permission has been obtained to visit some of the great factories in or near Birmingham, in which chemical and metallurgical industries are carried on. Students have thus had most valuable opportunities of gaining a practical acquaintance with some branches of Applied Science. The privilege thus courteously granted by several manufacturers will, it is hoped, be enjoyed in every future Session. The excursions will be conducted by the Professor or Lecturers.

CITY OF BRADFORD TECHNICAL COLLEGE.

Principal—Prof. W. M. Gardner, M.Sc.

Department of Chemistry and Dyeing.

Professor of Chemistry and Dyeing—W. M. Gardner, M.Sc., F.I.C.

Assistant Professor of Chemistry—B. North, A.R.C.S. (Lond.).

Lecturers in Chemistry—L. L. Lloyd, Ph.D.; H. Middleton, M.Sc.; N. Bland, M.Sc; A. Jackson, B.Sc.; S. F. Stell, F.C.S.

Lecturer in Physics—J. A. Tomkins, A.R.C.S. (Lond.).

Demonstrator in Physics—F. Harcourt, B.Sc.

Lecturers in Dyeing—A. B. Knaggs, F.C.S.; M. Fort, M Sc.

Lecturer in Gas Manufacture—W. Cranfield.

Lecturer in Botany, Biology, and Pharmacy—W. West, F.L.S., Past Pres. Yorkshire Naturalists' Union.

The following courses of instruction are provided—

I. *General Chemistry Course*, extending over four years, and including Lectures in Inorganic, Organic, and Technological Chemistry, Principles of Analysis, Technical Analysis, Electro-chemistry, Physical Chemistry, Crystallography, Fuels, Lighting and Ventilation, Physics, Mathematics, Mechanics, with Laboratory work in Chemistry, Physics, Bacteriology, and Microscopy.

II. *Chemistry and Dyeing Course*, extending over four years. Includes most of the above subjects, along with Lectures and practical work in Dyeing, Colour matching, &c. A completely equipped Practical Dyehouse and Finishing Rooms have now been added.

III. *Chemical Engineering*. Three years' course, preparing Students for positions in Chemical Works, Sewage Works, &c.

IV. *Sanitary Science.* One year's Course, recognised by the Sanitary Institute as preparing for their certificate examination. Subjects: Chemistry, Physics, Sanitary Engineering, Sanitary Law, Building Construction, Drawing, Physiology, and Bacteriology.

V. *Dyeing.* Special Courses for Graduates in Chemistry, and for Drysalters, Colour Merchants, &c.

VI. *Textile and Dyeing.* Arranged for those Students who desire to study the two subjects simultaneously.

VII. *First Professional Examination, Conjoint Medical Board (M.R.C.S., L.R.C.P.), London.*—Attendance at the College and College Certificates in Chemistry, Physics, and Biology are recognised by the Conjoint Board for Medical Studies as a qualifying curriculum.

VIII. *General Pharmaceutical Course.* Prepares for the Minor and Major Pharmaceutical Examinations. Each extends over two years on four half-days per week, and includes Chemistry and Physics, Botany, Biology, Materia Medica, Pharmacy, and Dispensing.

ROYAL AGRICULTURAL COLLEGE, CIRENCESTER.

Chemical Department.

Professor—Prof. E. Kinch, F.C.S., F.I.C.

Demonstrator—M. Kershaw, B.A., Ag.Dip. Cambs.

Assistant—H. Douglas Elkington, B.Sc., A.I.C.

Systematic courses of Lectures are given on the various branches of Chemistry in its relation to Agriculture, illustrated by experiments, and by the collections in the College Museum. They comprise the laws of Chemical Combination and the general Chemistry of mineral bodies, and of the more frequently occurring bodies of organic origin, with the relationships of their leading groups; and, finally, the applications to practical operations of the Chemistry of the atmosphere, of soils and manures, of vegetation, of stock feeding, and of the processes and products of the dairy.

In the Laboratory practical instruction is given in the construction and use of apparatus and in Chemical manipulation and analysis, both qualitative and quantitative. After studying the simple operations and the properties of the commonly occurring substances, the Students are taught to analyse a series of compounds, and apply the knowledge thus obtained to the analysis of manures, soils, waters, feeding stuffs, dairy products, and other substances met with in the ordinary course of Agricultural practice. Chemico-agricultural researches are undertaken by the senior Students under the direction of the Professor and his Assistants.

THE UNIVERSITY OF LEEDS.

Professor of Chemistry—Arthur Smithells, B.Sc., F.R.S.

Professor of Organic Chemistry—Julius B. Cohen, Ph.D., B.Sc., F.R.S.

Lecturer on Physical Chemistry—H. M. Dawson, D.Sc, Ph.D.

Assistant Lecturers and Demonstrators—W. Lowson, B.Sc., F.I.C.; W. H. Perkins, M.Sc., F.I.C.

Demonstrators—H. Calam, M.Sc., F.I.C.; J. Marshall, M.Sc.; H. S. Patterson, B.Sc.

Lecture Courses.

1. General Course of Chemistry.—Monday, Wednesday, and Friday, at 11.30 a.m. Fee for the Course, £5 10s.

2. Advanced Inorganic Chemistry. — (A) Monday, Wednesday, and Friday, at 9.30 a.m. Fee, £4 10s.

3. Advanced Inorganic Chemistry. — (B) Tuesday, Thursday, and Saturday, at 9.30 a.m. Fee, £4 10s.

4. Organic Chemistry. — Tuesday, Thursday, and Saturday at 12 noon Fee. £4 10s.

5. Honours Courses.—(*a*) Organic Chemistry: Monday, Wednesday, and Friday at 12 noon; fee, £4 10s. (*b*) History of Chemistry: Monday, Wednesday, and Friday at 9.30 a.m. in the First Term; fee, £2 5s. (*c*) Physical Chemistry: Monday, Wednesday, and Friday at 9.30 a.m. in the Second and Third Terms; fee, £3 7s. 6d. (*d*) Electro-chemistry: Tuesdays at 9.30 a.m.; £2 10s.

6. Chemistry of Food and Drugs.—Special class during the second term for Students taking Final Examination of the Institute of Chemistry in Branch E (Food and Drugs). £3 3s.

Laboratory Courses.

The University Laboratory will be open daily from 9 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it will close at 1 p.m.

Fees for the Session—£3 per half day of three hours per week.

Practical Course in Sanitary Chemistry.—Tuesdays and Thursdays from 2 to 5 from April to June. Fee, £5 5s.

Tinctorial Chemistry and Dyeing Department.

Professor—Arthur G. Green, M.Sc., F.I.C.

Lecturer and Research Chemist—A. G. Perkin, F.R.S. F.I.C.

Assistant Lecturer—G. H. Frank, M.Sc., F.I.C.

Demonstrator—A. Woodhead, M.Sc.

The Courses extend over periods of three or four years, and are intended for those who wish to obtain a full scientific and practical education in the art of dyeing, colour manufacture, &c. It is suitable for those who purpose in the future to take any part in the direction of the operations of dyeing or printing of textile fabrics, *e.g.*, the sons of manufacturers, calico printers, managers, master dyers, &c., or in the manufacture of coal-tar products and dyestuffs.

Leather Industries Department.

Professor—E. Stiasny, Ph.D.

Assistant Lecturers and Demonstrators—Harold Brumwell; W. R. Atkin, M.Sc.

The full Courses, which extend over a period of either two or three years, are suitable to all who intend to become Technical Chemists in the Leather Industry, or managers of important works, and are recommended to sons of tanners. The Courses include instruction in chemistry, a modern language, leather manufacture, and practical work in the Leather Industries Laboratory and Dye-house.

Agricultural Department.

Professor—R. S. Seton, B.Sc.

Lecturer in Agricultural Chemistry—C. Crowther, M.A., Ph.D.

The full Course occupies three years, and includes instruction in chemistry, physics, mathematics, geology, botany, forestry, engineering and surveying, and the principles of agriculture, as well as practical work in the various laboratories and out-door agriculture at the University Farm.

Department of Coal-gas and Fuel Industries with Metallurgy.

Livesey Professor—J. W. Cobb, B.Sc., F.I.C.

Assistant Lecturer and Demonstrator—H. J. Hodsman, M.Sc.

The Courses extend over two, three, or four years, and are suitable for those who are preparing for posts either as Gas Engineers or in Fuel and Metallurgical industries.

The Courses in Gas Engineering and the Technology of Fuel will chiefly deal with the manufacture and distribution of coal-gas and gas-lighting problems, by-product coking processes, and the production and application of gaseous fuels for heating and power purposes.

The Metallurgical Courses, besides dealing with general processes for the concentration and extraction of ores, will be chiefly directed to problems underlying blast furnace and open-hearth steel practice, and to the microstructure, physical properties, and heat treatment of steel and other industrial alloys.

Research Students are admitted to the University Laboratories on reduced terms.

Several valuable Fellowships and Scholarships are at the disposal of the University, including a Fellowship of £100 offered by the Institution of Gas Engineers, and the Salt, Akroyd, Brown, Baines, Emsley, Craven, and Clothworkers' Scholarships, and one of the 1851 Exhibition Scholarships. The Leeds City Council's and the North, East, and West Ridings County Council's Scholarships are tenable at the University of Leeds.

UNIVERSITY OF LIVERPOOL.

Professor of Inorganic Chemistry—E. C. C. Baly, F.R.S.

Professor of Physical Chemistry—W. C. McC. Lewis, M.A., Ph.D.

Professor of Bio-chemistry—Benjamin Moore, M.A., D.Sc., F.R.S.

Lecturer on Organic Chemistry—A. W. Titherley, D.Sc., Ph.D.

Lecturer on Metallurgy—Guy D. Bengough, D.Sc., M.A., A.R.S.M.

Assistant Lecturers and Demonstrators—A. J. Allmand, D.Sc.; F. D. Farrow, M.Sc.; Francis W. Kay, M.Sc., Ph.D.; A. Rule, M.Sc., Ph.D.; J. Smeath Thomas, M.Sc.

Lecture Assistant—H. H. Froysell.

The Session commences October 7th.

Entrance Scholarship Examination takes place early in May each year.

The Classes meet the requirements of candidates for the Ordinary B.Sc. Degree, for Chemistry Honours, or for the M.Sc. or D.Sc. Degree in the University of Liverpool; for Degrees in Medicine of Liverpool; for the Pharmaceutical, Veterinary, Dental, and Public Health Diplomas; and for those studying Chemistry as a preparation for professional, technical, or commercial life. The Classes qualify for the Fellowship of the Institute of Chemistry and other Examination Boards.

Lecture Courses.

A. General Introductory Course, including the principles of Organic, Physical, and Bio-chemistry. Three Terms. Fee, £4.

Engineer's Course of Lectures with Practical Class. Two Terms. Fee, including Practical class, £6.

Pharmacy Courses: Junior, £3; Senior, £3.

Course B.—Inorganic Chemistry. Fee, £3.

Course C.—Inorganic Chemistry (Honours Course). Fee, £2 10s.

Course D.—Organic Chemistry. Fee, £3.

Course E.—Organic (Honours). Fee, £4.

Course F.—Physical Chemistry. Fee, £3.

Course G.—Honours Physical Chemistry. Fee, £4.

Course H.—History of Chemistry and Chemical Philosophy. Fee, £2.

Course J.—Applied Inorganic Chemistry, including Metallurgy. Fee, £2.

Course K.—Applied Organic Chemistry. Fee, £2 10s.

Course L—Applied Electro-chemistry. Fee, £2 10s.

Also Pass and Honours Courses in Bio-chemistry.

Research students carrying out research work pay a fee of £3 per annum.

The Inorganic and Organic Chemical Laboratories provide accommodation for every kind of work and research in inorganic and organic chemistry and in metallurgy. There is also a laboratory devoted to spectroscopic work and research.

The Muspratt Laboratories of Physical Chemistry and Electro-chemistry adjoin the main chemistry buildings, and, owing to their full equipment, offer every opportunity or all manner of work and research in these subjects.

The Bio-chemical Laboratory is also separately housed, and provides facilities for work and research.

Students desirous of gaining a thorough theoretical and practical acquaintance with Technical Chemistry, or who intend to adopt Chemical work as a profession, must devote three or four years to special study, for which a full curriculum is provided. Fees:—

Per Week	One Term, Three Months.	Three Terms One Session
One day	£4	£7
Two days	5 10s.	10
Three days	7	13
Whole week	10 10s.	21

D.P.H. Course (see special syllabus).

Course for Dental Degree and Diploma (see special syllabus).

Technological Curriculum.

The curriculum extends over three or four years.

The Final Examination for the Associateship of the Institute of Chemistry may be taken after the third year. Those students who have taken the Ordinary Degree of B.Sc. may pass the M.Sc. Exam. in any subsequent year.

The Sir John Willox Scholarship of £50 per annum, tenable for two years, will be competed for in December, 1913, on an Examination in subjects which are included in the first two and a half years of the above curriculum. Candidates should send in their names to the Registrar not later than November 15. The Sheridan Muspratt Chemical Scholarship, on similar lines, is open for competition. Other Scholarships, Entrance Scholarships, and Free Studentships are also available to Students.

Evening Classes.

Classes on Metallurgy will be held during the winter.

Prospectuses containing particulars may be obtained from the Registrar, University of Liverpool.

ARMSTRONG COLLEGE, NEWCASTLE-ON-TYNE.

(In the University of Durham).

Professor of Chemistry—P. Phillips Bedson, M.A., D.Sc., F.I.C., F.C.S., J.P.

Lecturers in Chemistry—F. C. Garrett, D.Sc., F.C.S., and J. A. Smythe, D.Sc., Ph.D., F.C.S.

Assistant Lecturer and Demonstrator—A. A. Hall, M.Sc., Ph.D.

Demonstrators—A. Forster, M.Sc., Ph.D.; A. S. Blatchford, B.Sc.; and W. Wardlaw.

Lecturer in Agricultural Chemistry—S. Hoare Collins, M.Sc., F.I.C., F.C.S.

Assistant Lecturer in Agricultural Chemistry—G. S. Robertson, B Sc.

First Year Courses.—Division I.—This Course of Lectures will extend over the three terms of the Session, and is intended to serve as an introduction to the Science. The Lectures will be of an elementary character, and whilst framed to meet the requirements of First Year Students will also be serviceable to such as intend pursuing Chemistry in its various applications in the arts and manufactures, as, for instance, Brewing, Metallurgy, the Manufacture of Soda, Soap, Glass, &c. The subjects treated will include an exposition of the Principles of Chemistry, and a description of the preparation and properties of the chief Elementary Substances, both metallic and non-metallic, and their more important native and artificial compounds. The class will meet on Mondays, Wednesdays, and Fridays, at 11 a.m., and will commence on Wednesday, October 9th. Fee, £3 10s. for the Session.

Division II. Similar to Division I., but modified to meet requirements of Students for Degrees in Engineering and Mining. Mondays 12 to 1, Tuesdays and Thursdays 10 to 11. Fee, £3 10s. for Session.

Second and Third Year Courses.—These lectures are designed to form a part of the course of instruction in Chemistry, and to prepare students for the examinations in Chemistry for the degree of Bachelor of Science, Pass and Honours.

(*a*) Inorganic Chemistry.—Advanced Course, Tuesdays and Thursdays at 11 a.m. Fees, Lectures, £3 10s. per session, and £1 10s. per term.

(*b*) Organic Chemistry.—Aliphatic and Aromatic Compounds, Tuesdays and Thursdays at 10 a.m. Fees, Lectures, £3 10s. per session; £1 10s. per term.

(*c*) Organic Chemistry.—Advanced Course, Tuesdays and Thursdays at 12 noon for part of the session. Fees, Lectures, £3 10s. per session; £1 10s. per term.

(*d*) History of Chemistry and Chemical Philosophy.—Saturdays at 10 a.m. Fees, Lectures, £3 10s. per session; £1 10s. per term.

(*e*) Physical Chemistry.—Tuesdays and Thursdays at 12 noon for part of the session. Fees, Lectures, £3 10s. per session; £1 10s. per term.

(*f*) Analytical Chemistry.—Fridays at 9.15 a.m. Fee, £1.

(*g*) The Rarer Elements and the Periodic Law.—Times to be arranged. Fees, Lectures, £3 10s. per session; £1 10s. per term.

Students taking Chemistry for Pass Degree will attend in their second year the course *a* and *f*, and in their third year the courses *b* and *d*, in addition to the necessary Laboratory practice.

Students taking Chemistry for Honours Degree will attend in their second year the courses *a*, *b*, and *f*, and in their third year the courses, *c*, *d*, *e*, and *g*, in addition to the necessary Laboratory practice.

A Lecture Course in Analytical Chemistry will be given on Fridays, at 9.15 a.m. Fee for the course, £1.

Metallurgy and Assaying.—Lecturer, Prof. Louis, M.A., D.Sc., F.I.C., F.G.S.; Demonstrator, H. Dean, M.Sc., A.R.C.M.; G. H. S. Kent. A Metallurgical Laboratory is provided, in which instruction is given in the ordinary processes of Dry Assaying, and in the preparation and analysis of Alloys, &c. Fees as for Chemical Laboratory.

Agricultural Chemistry.—The instruction in this branch of Chemistry will consist of a series of Lectures and of special practical work in the Chemical Laboratory. Students will be expected to have a knowledge of Elementary Chemistry, such as may be obtained by attending the General Course.

The Lecture Course in Agricultural Chemistry is arranged for two days a week throughout the Session. Fee, £3 10s.

Practical Chemistry.—The Laboratory is open from 10 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it closes at 1 p.m. *Laboratory Fees.*—Students working six days per week £5 10s. per term, £15 per session; one day per week, £2 per term, £5 per session.

Courses of Study.—Students will be divided into two classes:—(1) Regular, or Matriculated Students, who are also Members of the University of Durham; and (2) Non-Matriculated Students. Regular Students will be required to follow such a course of study in the subjects professed in the College as will enable them to pass the Examinations for the degree of Bachelor in Science of the University of Durham. Non-Matriculated Students will attend such classes as they may select. Every candidate for admission as a matriculated student must have passed the University Matriculation Examination.

Matriculation Examination.—In order to enter on a course of study for a Degree a student must have previously satisfied the Examiners in the following subjects:—(1) English, (2) English History, (3) Mathematics, (4) three of the following subjects, of which one must be a language:—(*a*) Religious Knowledge, (*b*) Latin, (*c*) Greek, (*d*) Ancient History, (*e*) French, (*f*) German, (*g*) some other language to be approved, (*h*) Experimental Science or Physics or Chemistry, (*i*) Botany or Zoology, (*j*) Mechanics, (*k*) Extra Mathematics, (*l*) Geography.

(i.). Candidates for degrees in Arts, who do not offer Latin in their Matriculation Examination or in the equivalent accepted as exempting therefrom, will be required to pass in Latin at a subsequent examination before entering upon the Arts course.

(ii.). Candidates for degrees in Commerce, who do not offer a Modern Foreign Language in their Matriculation Examination, or in the equivalent as exempting therefrom, will be required to pass in a Modern Foreign Language at a subsequent examination before entering upon the Commerce course.

(iii.). Candidates for degrees in Engineering (Civil, Mechanical, and Electrical) and in Naval Architecture will be required to take the following subjects from the list:—(1) English; (2) English History; (3) one of four languages—Latin, Greek, French, German; (4) Experimental Science; (5) Extra Mathematics; (6) Geography.

(iv.). Foreign Students may be exempted from the

Matriculation Examination on report from the Board of Professors of Armstrong College, that they have received such an education in their own country as will enable them to profit by University study, and that they have sufficient knowledge of English to enable them to follow the courses of instruction they are entering for.

For detailed Syllabuses and complete Regulations the College Calendar should be consulted.

Bachelorship in Science.—The degree of Bachelor of Science is conferred in Pass and Honours in Pure and Applied Science. For details of curricula, &c., the College Calendar should be consulted.

Exhibitions.—Two Exhibitions of the value of £20 and £10 respectively will be awarded in October next to Candidates desirous of attending the first year course of study in the College.

The examination will be held at the College, and will commence on Thursday, October 2nd, 1913. Candidates should send in their names to the Secretary on or before September 12th.

Evening Lectures.—Under the auspices of the College and the Newcastle Section of the Society of Chemical Industry, special Courses of Evening Lectures will be given—Course of 5 Lectures by Prof. Cobb, Fuel Economy, to commence in October 1913, and a Course of 5 Lectures commencing January, 1914, to be announced later.

Several valuable Scholarships are available for students, including the Johnston Chemical Scholarship of the value of £60 for one year, which is open to Bachelors of Science of any British University; the examination for this Scholarship will be held during the week commencing September 30th. Candidates should send in their names to the Secretary on or before September 22nd.

THE UNIVERSITY OF MANCHESTER.

Professor of Chemistry and Director of the Chemical Laboratories—Harold B. Dixon, M.A., M.Sc., Ph.D., F.R.S.

Professor of Organic Chemistry—Arthur Lapworth, D Sc, F.R.S.

Reader in Biochemistry and Senior Lecturer in Chemistry—C. Weizmann, Ph.D., D.Sc.

Senior Lecturers and Demonstrators—Norman Smith, D.Sc.; E. C. Edgar, D.Sc.; and F. P. Burt, D.Sc.

Assistant Lecturers and Demonstrators—F. R. Lankshear, B.A., M.Sc.; Edward Hope, M.Sc.; J. E. Myers, M.Sc.; Jacob Jones, M.Sc.; and J. R. Partington, M.Sc.

Professor of Metallurgy—H. C. Carpenter, M.A., Ph.D.

Assistant Lecturer in Metallurgy—J. H. Andrew, M.Sc.

Lecturer in Electro-Chemistry—J. N. Pring, D.Sc.

The Session begins October 1st, 1913.

Chemistry Lecture Courses.

General Chemistry Course.—Tuesdays, Thursdays, and Saturdays, at 9.30, during the two Winter Terms.

This course is intended for Students commencing the study of chemistry.

Introduction to Organic Chemistry.—Mondays, Wednesdays, and Fridays, at 11.30, during the Summer Term.

This course is designed to meet the requirements of Students preparing for the Intermediate B.Sc. Examination.

Biochemistry, Theoretical and Practical—Tuesdays and Thursdays during the Summer Term. This Course prepares for Part III. of the first M.B. Examination.

First Year Honours Course.—Mondays, Wednesdays, and Fridays, 11.30, during the two Winter Terms. The Non-Metals.

Second Year Honours Course.—Mondays, Wednesdays, and Fridays, at 2, during the two Winter Terms. The Metals.

Third Year Honours Course.—Theoretical and Physical Chemistry.

Organic Chemistry (General).—Mondays and Fridays, at 9.30, during the two Winter Terms.

Organic Chemistry (Advanced).—Tuesdays and Wednesdays, at 9.30, during the two Winter Terms.

History of Chemistry.—Short Courses during the two Winter Terms.

Chemistry of Colouring Matters—Theoretical and Practical Course during the Winter Terms.

Metallurgy.—Introductory Course, followed by either—(A) Lead, Copper, Bismuth, Antimony, Zinc, and Tin; or (B) Iron and Steel. Each Course, one Lecture per week during the Session.

Electro-chemistry.—General Theoretical Course: One hour per week during the Michaelmas and Lent Terms. Applied Course: One hour per week during Michaelmas and Summer Terms.

B.Sc. with Honours in Chemistry.—The course extends over three years, and comprises systematic instruction by means of lectures and practical work in the laboratories.

The Research Laboratories for Inorganic, Organic, and Physical Chemistry, and for Metallurgy, are open to graduates and other advanced students.

For further particulars of any of these courses apply to the Registrar, Edward Fiddes, M.A., or to the Director of the Laboratories.

UNIVERSITY COLLEGE, NOTTINGHAM.

DEPARTMENTS OF CHEMISTRY AND METALLURGY.

Professor of Chemistry—F. Stanley Kipping, Ph.D., D.Sc., F.I.C., F.R.S.

Demonstrators of Chemistry—R. M. Caven, D.Sc., F.I.C.; G. Sand, D.Sc.; and H. Lambourne, B.Sc.

The Classes of the College are open to students of both sexes above sixteen years of age.

Lecture Courses.—The Chemistry Day Lectures extend over three years. In the first year a student attends a course on Inorganic Chemistry. In his second year he attends Lectures on both Inorganic and Organic Chemistry. In his third year he attends courses on Advanced Organic Chemistry, Physical Chemistry, and Advanced Inorganic Chemistry.

Demonstrations and Lectures on Analytical Chemistry are given, and Chemical Calculation and Tutorial classes are also held. Various short courses of lectures on special subjects are delivered during the Session.

Students may qualify themselves by attendance at these lectures and classes for the Examinations of the Universities of London, Cambridge, or Oxford, and for the Medical Examinations of the Royal College of Surgeons and of the Universities of Cambridge and Edinburgh: they may also obtain instruction in Chemistry for technical or other purposes, and can enter for a full Chemical Engineering Curriculum. Special attention is given to the requirements of candidates for the Associateship of the Institute of Chemistry.

Practical Chemistry and Metallurgy.—The Chemical and Metallurgical laboratories are open every day from 9 to 5, except on Saturday, when the hours are from 9 to 1; also on Tuesday and Thursday evenings from 7 to 9. Each Student works independently of other Students at a course recommended by the Professor. Instruction is given in general Chemical Manipulation, in Qualitative and Quantitative Analysis, and in the methods of Original Chemical Investigation and Research; Students are also enabled to work out the applications of Chemistry to Pharmacy, Metallurgy, Dyeing, Brewing, Iron and Steel, and other Manufacturing Processes.

Research Work.—Students or others wishing to undertake research work in pure or Applied Chemistry will be afforded every facility for doing so and may be admitted at reduced fees. The Laboratories are fully equipped with apparatus and chemicals necessary for such work.

Courses of Technical Chemistry Lectures are also given on Engineering, Dyeing and Bleaching, Brewing, Plumbing, Gas Manufacture, and on other processes of applied Chemistry.

Pharmaceutical Students are provided with Lectures and Laboratory work suitable for the preparation for the Minor and Major Examinations.

The composition fee for full time in the Chemistry

Department (lectures and laboratory) is £6 per term, and this fee covers all necessary apparatus and chemicals.

A composition fee of £6 per term is also charged for various complete courses, such as those required for the Institute of Chemistry, and for the degree examinations of London University.

Evening Classes.—Evening Lectures and Laboratory instruction will be given in Pure and Applied Chemistry, and the laboratories are open for practical work on Tuesday and Thursday evenings from 7 to 9. Fee for each Lecture Course, 5s.; for each Laboratory Course, 10s.

Full information concerning all College Classes is given in the College Prospectus, free from the Registrar.

THE UNIVERSITY OF SHEFFIELD.

Professor of Chemistry—W. P. Wynne, D.Sc., F.R.S.

Lecturers and Demonstrators—W. E. S. Turner, D.Sc., M.Sc.; W. J. Jarrard, B.Sc.; C. R. Young, B.Sc.; J. Kenner, Ph.D., B.Sc.

The Session will commence October 1st.

Matriculation Course. — Tuesday and Friday at 9.30. Fee, £2 12s. 6d., and three hours per week Laboratory work.

Candidates for the Intermediate Examination are required to satisfy the Examiners in three of the following subjects:—Pure Mathematics, Applied Mathematics, Physics, Chemistry, Zoology, and Botany. And those for the Final Examination in three of the following subjects:—Pure Mathematics, Applied Mathematics, Physics, Chemistry, Zoology, Botany, Physiology, Geology, Education.

Intermediate Course in Chemistry for B.Sc. or M.B., Ch.B.—Monday, Wednesday, Thursday, and Saturday at 9.30 a.m. £5 5s., and six hours per week Laboratory work during first year.

B Sc. Course in Chemistry.—Monday at 9.30 a.m. and Tuesday at 12.30 p.m. during second year, £3 3s.; Wednesday at 12.30 a.m., during two terms, Thursday at 10.30 a.m. and Friday at 10 30 a.m., during third year, £3 3s.; and nine hours per week Laboratory work during second and third years.

B.Sc. with Honours.—Honours Students in Chemistry, after passing the Intermediate Examination, devote the whole of their time to the study of Chemistry, and are expected to reach the standard for a pass in Chemistry for the ordinary degree by the end of the second year. During the second or third year they devote one day a week to lectures and practical work in a subsidiary subject—Mathematics, Physics, or Metallurgy—selected for the degree. The third year is devoted to the advanced study of Chemistry, either chiefly Physical and Inorganic or chiefly Organic, as the student may select. At least four days a week during the second and third years are spent in the laboratory.

M.Sc.—This degree may be conferred upon a Bachelor of Science with Honours who is of one year's standing from the date of his graduation as a Bachelor of Science, or upon a Bachelor of Science who has either passed an examination in an Honours School subsequent to graduation, or has for at least one year after graduation done research work at the University, and has presented a thesis, approved by the Faculty of Pure Science, upon the research work done during that period.

D.Sc.—The degree of Doctor of Science may be conferred upon any Master of Science of not less than five year's standing from the date of his admission to the degree of Bachelor, provided that he has published, in recognised journals or transactions, a research or researches of special merit and approved by the Faculty of Pure Science as qualifying him for the degree.

Laboratory.—Working hours to be arranged between Professor and Students.

Sessional Fees for Day Students:—Three hours per week, £3 3s.; Six, £5 5s.; Nine, £7 7s.; Twelve, £9 9s.; Eighteen, £12 12s.; Twenty-four, £14 14s.; Thirty-two, £16 16s.; Honour or University Students taking eighteen hours or more per week, £12 12s.

Students joining the Laboratory for one term are charged one half, and for two terms two-thirds of the Fees for the whole Session.

A Course of Lectures, with a special class in Laboratory Work, is arranged for Medical Students entering for the Conjoint Board Examinations. Fee, £7 7s.

A course of Practical Chemistry which meets the requirements of candidates for the Diploma of Public Health is held during the Michaelmas and Lent terms. Fee, £6 6s.

An arrangement has been entered into with the Board of Education, London, S.W., which will enable Science Teachers to work in the Chemical Laboratory for three, six, or twelve hours a week on payment of one-quarter of the usual fee, the Board being willing to pay the remainder under certain conditions, of which full information may be obtained on application to the Registrar of the University.

Evening Classes.—Lecture Class and Laboratory, on Thursday evening during the Michaelmas and Lent terms. Fee, £1 10s.

Department of Metallurgy.

Professor—J. O. Arnold, D.Met., F.R.S.

Senior Lecturers—F. K. Knowles, B.Met.; F. Ibbotson, B.Met., B.Sc.

Lecturer—J. H. Wreaks, B.Met.

Lecturer in Non-ferrous Metallurgy—G. B. Brook.

Lecturer in Electro-metallurgy—W. R. Barclay, A.M.I.E.E.

This Department has been equipped to meet the requirements of the local industries. The Laboratory is fitted with the most modern apparatus for metallurgical analysis, more especially with appliances for the rapid and accurate chemical examination of iron and steel, fuel, and refractory materials. It also contains a complete pyrometric installation, and a laboratory for the study of the micrographic analysis of metals fully equipped with specially designed microscopes by Ross, polishing tables, etching appliances, incandescent light for evening work, &c. The Department is now most complete for teaching the practical manufacture, the chemical constitution, and the physical properties of steel. Special attention is given to the determination of the microscopic constituents of steel. Although the chief industry of the district occupies the central position in the course of instruction, general metallurgy is not neglected, but is dealt with in a separate syllabus, dealing with metals (other than iron and steel) used in the arts. Students are thus enabled to select and at once enter upon a course of scientific metallurgical training of immediate practical utility. They may take up and work through any portions of the course, but certificates are granted only to those who follow the prescribed courses and pass the necessary examinations. Lectures on Iron and Steel Manufacture, on Fuel and Refractory Materials, and on General Metallurgy. Practical Metallurgy:—Laboratory, Furnaces, Foundry, and Testing Machine Course; Practical Course of Metallurgy other than Iron and Steel; Practical Fuel Course for Students in Collieries or Gas Works.

A steel works has been erected in connection with the Sheffield University at a cost of about £15,000, with a most varied and complete plant. The most recent addition to the steel works plant is a 3 cwt. Kjellin induction furnace worked by a 120 H.P. Motor-generator set with two-phase current. The Metallurgical Department of Sheffield University is "in association" with the Royal School of Mines for teaching the advanced metallurgy of Iron and Steel.

There has been recently added to the curriculum Day and Evening courses in Electro-metallurgy and Non-ferrous Metallurgy. The Electro-metallurgical Laboratory is completely equipped for the practical study of every branch of the art of the Electro-deposition of metals, special attention having, however, been paid—in the selection and arrangement of plant and apparatus—to the specific requirements of the Sheffield trades. The plant and machinery is thoroughly up-to-date in character.

Working accommodation is provided for 30 students at one time, and the course extends over three university years.

The Non-ferrous Department has been established to meet the needs of the lighter Sheffield trades of Silver and Electro-plate, Brass, and allied industries. It is completely equipped for dealing with every phase of the work from the raw material. The melting shop is fitted with furnaces capable of dealing with casts up to 70 lbs. weight, so that commercial practice can be followed. Two large laboratories, the one with 32 places for preparatory students, the other with accommodation for 40 advanced students, provide the means for the Chemical examination of the alloys prepared. A Staff and Post-graduate research laboratory completes the provision for the chemical side of the work. The Micrographic Laboratory is equipped with a complete Zeiss Photo-micrographic camera, direct driven polishing blocks, and Ross microscopes. The recalescence laboratory for the estimation of temperatures during melting, annealing, or other heat treatment has a complete pyrometric installation. An Arnold and Colver-Glauert Pyrometer permits of readings every 1° C. up to 1300° C. Facilities are provided for observing the thermal changes *in vacuo*. The Chronographic recorder is served by electric or coke furnaces, and the installation may be regarded as the most complete of its kind.

UNIVERSITY COLLEGE, READING.

Professor of Chemistry—H. Bassett, D.Sc., Ph.D., D. ès Sc., F.I.C.

Lecturers—J. W. Dodgson, B.Sc.; A. E. Everest, M.Sc.

Professor of Agricultural Chemistry—S. J. M. Auld, D.Sc., Ph.D., F.I.C.

Research Chemist in Dairying—J. Golding, F.I.C.

Lecturer in Agricultural Chemistry—J. A. Murray, B.Sc.

The lectures and laboratory work are so arranged as to be suitable for students preparing for the London B.Sc. (Pass or Honours), or for the College or other Diplomas in Agriculture, Horticulture, or Dairying. There is a general course of Intermediate standard, also another suitable for first year students of Agriculture and Horticulture. In their second and third years Science students attend special lectures in Inorganic, Organic, and Physical Chemistry, while Agricultural students take special courses under the Professor of Agricultural Chemistry. The laboratories are well equipped for all branches of practical work.

Halls of Residence—(Men) Wantage Hall, St. Patrick's Hall; (Women) St. Andrew's Hall, Wessex Hall, St. George's Hostel.

Full details of fees, scholarships, &c., can be obtained from the Registrar.

UNIVERSITY COLLEGE, DUNDEE.

UNIVERSITY OF ST. ANDREWS.

Professor of Chemistry—Hugh Marshall, D.Sc., F.R.S.

Assistant Lecturers—J. K. Wood, D.Sc. and (Vacant).

Lecture Assistant and Lab. Steward—J. Foggie, F.C.S.

The Session consists of three Terms:—The Martinmas Term begins early in October and ends before Christmas; the Candlemas Term begins early in January and ends about the middle of March; the Whitsunday Term begins in the middle of April and ends at the end of June.

Three Courses of Lectures are given, each extending through all three terms. The Junior Course, meeting four or five days a week (including Tutorial Meetings), is intended for beginners, and qualifies for Graduation Examinations in Arts (M.A. General), Science (First B.Sc.), and Medicine (First Professional).

The Intermediate and Advanced Courses, each meeting twice or thrice weekly, qualify for Degree Examinations in Arts (Special and Honours, respectively), and in Science (Final B.Sc. on Intermediate and Higher Standard, respectively).

All three are General Courses, including Inorganic, Physical, and Organic Chemistry.

The Laboratories are well equipped, and instruction is provided for students in Arts, Science (Pure and Applied), Medicine (including Public Health); provision is also made for students desiring to undertake Technological Work or Research.

UNIVERSITY OF ABERDEEN.

CHEMISTRY.

Professor—Francis R. Japp, M.A., LL.D., F.R.S.

Lecturer on Physical Chemistry—Francis W. Gray, M.A., D.Sc.

Demonstrators—Joseph Knox, D.Sc.; W. H. T. Williamson, B.Sc.

I. *General Lecture Course* (100 *Lectures*).—Daily during the Winter Session. The subjects treated of include (1) The Laws of Chemical Combination and the General Principles of Chemistry; (2) Non-metallic and Metallic Elements, and their Compounds; (3) Organic Chemistry; (4) Applications of Chemistry to the Arts and Manufactures. Fees, for first attendance, £4 4s.; for subsequent attendance, £3 3s. A Tutorial Class (without fee), conducted by the Junior Demonstrator, is held in connection with this course.

II. *Physical Chemistry* (60 *Lectures*).—Three Lectures a week on Physical Chemistry, with Practical Demonstrations, are delivered during the Winter Session by the Lecturer, Dr. F. W. Gray. Fee, £2 2s.

III. *Inorganic Chemistry* (40 *Lectures*).—Two Lectures a week on Advanced Inorganic Chemistry are delivered during the Winter Session by the Lecturer, Dr. J. Knox. Fee, £2 2s.

IV. *Special Lecture Course on Organic Chemistry* (50 *Lectures*).—Daily during the Summer Session. Fee, £3 3s.

V. *Practical Course for Medical Students*.—This course, which occupies five hours a week during the Summer Session—in all fifty hours—is devoted to practice in Elementary Qualitative Analysis. Fee, £3 3s.

VI. *Chemical Laboratory*.—The Laboratory is open to Students daily from 9 a.m. to 5 p.m. Each Student on entering is allowed to arrange his hours of work so as to suit his own convenience, but must adhere to these hours when once fixed. The Laboratory instruction includes: (1) General experiments; (2) Preparations; (3) Qualitative analysis; (4) Quantitative analysis: gravimetric, volumetric, and gasometric. The Course qualifies for the examinations of the Institute of Chemistry. Fee, £3 3s. a session. A certain number of free places are available, on the recommendation of the Professor, and subject to the approval of the Senatus, for research students.

UNIVERSITY OF ABERDEEN AND ABERDEEN AND NORTH OF SCOTLAND COLLEGE OF AGRICULTURE.

Agricultural Chemistry.

Professor—James Hendrick, B.Sc., F.I.C.

Assistants—R. Glegg, B.Sc., F.I.C.; Alfred Hill, B.Sc.

I. Preparatory Courses in General Chemistry and in Organic Chemistry are given for those who are unable to take the full University Courses in these subjects. The course in General Chemistry consists of about sixty Lectures with Practical Work (one hour daily) during the Winter Session. The course deals with the general principles of Chemistry, and with those parts of Inorganic Chemistry which are of more immediate concern to students of Agricultural Chemistry. The Practical Work goes along with and illustrates the Lectures. Fee, £4 4s.

The course in Organic Chemistry consists of about thirty Lectures, and is given during the Winter Session. It deals especially with those parts of the subject which are directly related to Agricultural Chemistry. Fee, £1 1s.

II. *Agricultural Chemistry* (*General Course*).—This class meets daily during the Winter Session, and includes both Lectures and Laboratory Work. The Lectures deal with the Chemistry of the Atmosphere, the Soil, Manures, Foods, Preservatives, Insecticides, &c. The Physiological

Chemistry of Plants and Animals, the Composition and Manurial Requirements of Crops, and Dairy Chemistry are also treated of. The Laboratory Work is primarily intended to accompany and illustrate the Lectures. Exercises dealing with the properties and composition of Soils, Manures, Feeding-stuffs and Waters, and with the impurities and adulterations of these, occupy much of the time given to Practical Work. The fee for the whole Course (Lectures and Practical Work) is £4 4s.

III. *Laboratory.*—A Summer Course in Practical Chemistry is given to prepare students who have not previously done sufficient laboratory work for the course in Agricultural Chemistry. Fee, £2 2s.

IV. The Laboratory is open daily from 9 a.m. to 5 p.m. for students who wish to study the principles and practice of Agricultural Chemistry or to undertake research in this subject.

UNIVERSITY OF EDINBURGH.

DEPARTMENT OF CHEMISTRY.

Professor—James Walker, LL.D., D.Sc., Ph.D., F.R.S.

Lecturers—L. Dobbin, Ph.D.; A. C. Cumming, D.Sc.; W. W. Taylor, M.A., D.Sc.; and J. E. Mackenzie, Ph.D., D.Sc., and six Demonstrators.

The three working terms are each of ten weeks' duration, viz.:—Autumn term, October to December; Spring term, January to March; Summer term, April to June.

Lecture Courses.—During the Winter Session a General Course of Chemistry for medical students is given. The class meets daily; fee, £4 4s. The First Course for Arts and Science students meets three times a week throughout the year; fee, £4 4s. The Second Course is given on Organic, Advanced Inorganic, and Physical Chemistry. The class meets three times a week throughout the year; fee, £4 4s. Tutorial Classes are held in connection with the First and Second Courses. All Arts and Science Classes are open to Women Students.

In addition to the above, Advanced Lecture Courses are given on particular branches of Physical, Organic, and Inorganic Chemistry.

Laboratories.—Practical classes for Medical Students meet during the Winter Session and in the Summer Session. (Fee, £3 3s.). The Elementary Laboratory course for Arts and Science students is held for four hours per week during the year. Fee, £4 4s. The advanced laboratories for Science and Arts Students engaged in analytical and advanced practical work are open daily from 9.30 till 4.30. Fees: Whole Day—Year, £16 16s.; one term, £6 6s. Half Day—Year, £8 8s.; one term £3 3s. Full Courses of instruction are given in Analytical, Practical Organic and Inorganic Chemistry (including Gas Analysis, Physico-chemical Measurements, and Assaying). Facilities are afforded to advanced students who desire to undertake chemical investigations.

Various prizes and scholarships are attached to the laboratory and general class.

Graduation.—Two Degrees in Pure Science are conferred, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.).

Candidates for Degrees in Science, if not graduates (by examination) in Arts in one of the Universities of the United Kingdom or in a Colonial or Foreign University recognised for the purpose by the University Court, must pass a preliminary examination in (1) English; (2) Latin, Greek, French, or German; (3) Mathematics; (4) One of the languages Latin, Greek, French, German, Italian, not already taken under (2), or Dynamics. In the case of a student whose native language is other than European, the Senatus may, at the Preliminary Examination, accept such language as a substitute for a modern European language. The Senatus may also in such a case accept as an alternative to Latin or Greek any other classical language, such as Sanscrit or Arabic.

The First B.Sc. Examination embraces Mathematics, or Biology (*i.e.*, Zoology and Botany), Natural Philosophy, and Chemistry. The Final B.Sc. Examination in Pure Science includes any three or more of the following subjects:—Mathematics, Natural Philosophy, Astronomy, Chemistry, Human Anatomy (including Anthropology), Physiology, Geology (including Mineralogy), Zoology (including Comparative Anatomy), and Botany (including Vegetable Physiology). In the Final Examination two written papers are set in each subject professed, the second of a higher standard than the first. Candidates must pass the first section in all, and the second section in at least one, of the subjects professed; the same regulations apply also to the Practical and Oral Examinations. Chemistry in this examination embraces Inorganic Chemistry, Organic Chemistry, and Physical Chemistry. Practical Examination:—Complex Qualitative Analysis; Preparations; Gravimetric and Volumetric Analysis; Testing of Organic Substances. Each candidate taking the higher standard will also be examined on Ultimate Organic Analysis; Gas Analysis; Assaying; and Physico-chemical Measurements.

A candidate for the D.Sc. Degree must submit a thesis on original work done by him. The Thesis must be approved before the candidate is allowed to proceed to Examination. The candidate in Chemistry *may be* required to pass a searching examination in one of the following branches:—(1) The Chemistry and Chemical Technology of Inorganic Bodies, including Metallurgy; (2) Organic Chemistry; and to show a thorough practical acquaintance with chemical analysis in all its branches, and with the preparation of pure substances.

HERIOT-WATT COLLEGE, EDINBURGH.

Principal—A. P. Laurie, M.A., D.Sc., F.R.S.E.

Professor—John Gibson, Ph.D., F.R.S.E.

Assisted by the following Lecturers and Demonstrators:—A. Archibald Boon, B.A., D.Sc.; Andrew King, F.I.C.; F. D. Miles, B.Sc.; and Clerk Ranken, D.Sc.

The curriculum of this College comprises both Day and Evening Classes, each department providing the higher general and technical education.

The Chemistry Course is designed to meet the wants of Analytical and Manufacturing Chemists. The instruction consists of Courses in Chemistry, Physics, Mathematics, Engineering, and Mechanical Drawing, with Special Courses in Gas and Paper Manufacture, Brewing, &c., by Experts, in the fourth year. Special attention will be paid to Electrochemistry. The Chemistry Classes are recognised by the University of Edinburgh as qualifying for the B.Sc., in Chemistry, and are also recognised by the Institute of Chemistry.

For Students who have been three and four years in the Chemistry Department, arrangements have been made for their spending from four to twelve months in the laboratories of the Corporation's Gas Works, with a view to the study of problems connected with the Combustion of Fuel, the Manufacture of Coal-gas and its By-products, &c.

A Laboratory, under the charge of Prof. Emil Westergaard, has been provided for the study of Technical Mycology, including Brewing, Distilling, Malting, Vinegar Making, Tanning, Preserving, Starch and Sugar Making, Bread Making, Butter and Cheese Manufacture, &c.

Day Classes open on October 7th, and the Evening Classes on September 29th.

Matriculation Fee, 5s.; Composition Fees from £12 12s. to £15 15s. Full particulars are published in the Calendar of the College, which is issued early in September.

THE ROYAL TECHNICAL COLLEGE, GLASGOW.

Professor of Chemistry—G. G. Henderson, D.Sc., M.A., LL.D.

Professor of Technical Chemistry—T. Gray, D.Sc., Ph.D.

Lecturer on Dyeing—A. B. Steven, B.Sc.

Lecturer on Sugar Manufacture—T. H. P. Heriot, F.C.S.

Professor of Metallurgy—A. Campion, F.I.C., F.C.S.

Also, Professors and Lecturers in the other leading branches of Pure and Applied Science and Technology.

Session opens Sept. 23.

The main object of this College is to afford a suitable education to those who wish to qualify themselves for following an industrial profession or trade. It was founded by an Order in Council, dated November 26th, 1886, according to a scheme framed by the Commissioners appointed under the provisions of the Educational Endowments (Scotland) Act, whereby Anderson's College (established 1796), the Young Chair of Technical Chemistry in connection with Anderson's College, the College of Science and Arts, Allan Glen's Institution, and the Atkinson Institution were placed under the management of one governing body.

The Diploma of the College is awarded to Day Students who have attended prescribed courses of instruction and passed the necessary examinations. The ordinary courses extend over three years, but arrangements are made for advanced students continuing their studies in special departments. The diploma course in Chemistry extends over four years.

Students who have matriculated at the University of Glasgow can qualify for the degree of B.Sc. in Applied Science by attendance on the Day Classes of the College.

Complete courses of instruction are provided in both Day and Evening Classes.

Copies of the Calendar for 1913-1914 may be had from the Director, Mr. H. F. Stockdale; price by post, 1s. 4d. Prospectuses will be sent free.

UNIVERSITY OF ST. ANDREWS.

UNITED COLLEGE OF ST. SALVATOR AND ST. LEONARD

Professor of Chemistry—James C. Irvine, Ph.D., D.Sc.

The Session begins on October 13th. A Competitive Examination, open to intending Students of Arts, Science, and Medicine, for about thirty-seven Bursaries, ranging in value from £50 to £10 each per annum, will be held on September 12th and following days. Twenty-two of these Bursaries are restricted to Men, one is open to Men or Women, and fourteen are restricted to Women, the latter being intended for women who at the conclusion of their Arts or Science Course will proceed to Medicine.

A Hall of Residence is provided for Women Students.

Two Degrees in Science are conferred by the University of St. Andrews, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.), and Chemistry is also included in the curriculum for the M.A. Degree, and the M.B., Ch.B. Degrees; the regulations will be found in the "University Calendar."

Lecture Courses.

Three distinct Courses of Lectures are given, each extending over the three terms of the academic year.

First Year's Course.—This Class meets at 11 o'clock on five days in the week. The introductory lectures treat of the Nature of Chemical Action, the Classification of Substances into Elements and Compounds, the Phenomena of Oxidation, and the Composition of Air and Water. The Laws of Chemical Combination and the Atomic Theory are next discussed, after which the more commonly occurring elements and inorganic compounds are described systematically. Elementary Organic Chemistry is also included in the Course.

The chemistry of manufactures is referred to only cursorily; special attention, on the other hand, is given to those parts of the science which are of general educational value, and as much of the theory of chemistry is introduced as is compatible with elementary treatment.

This course of instruction is intended to meet the requirements of the M.A., First Science, and M.B., Ch.B. Exams., so far as Theoretical Chemistry is concerned.

Second Year's Course.—The first part of the Course is devoted to Organic Chemistry, and the second part to General and Physical Chemistry, the instruction in general being such as is required for the Final Science Exam. on the Lower Standard and the Special Exam. for the M.A. Degree.

Third Year's Course.—Short courses of lectures on selected topics are given to Students preparing for the B.Sc. on the Higher Standard or the M.A. Degree with Honours.

Certificates are awarded on the results of examinations, and the "Forrester Prize" of about £10 is awarded to the best Student of the year.

Fee for the Session, for each Course, £4 4s.

Practical Chemistry.

The Laboratory is open daily from 9 a.m. to 4 p.m., except on Saturdays, when it is closed at 1 p.m. The work pursued in the Laboratory comprises:—(1) The performance of experiments illustrative of the Principles of Inorganic and Organic Chemistry; (2) Qualitative and Quantitative Analysis; (3) Practical Physical Chemistry. Each student pursues an independent course of study under the supervision of the Professor or Demonstrator, the nature of the work varying with the proficiency of the student and the particular object he may have in view. Suitable courses of instruction in Practical Chemistry are provided for candidates for the Exams. in Arts, Science, and Medicine.

The fee for the Ordinary Course of Practical Chemistry is £3 3s, and for the Advanced Course £10 10s.

Original Research.

A special Research Department has been instituted by the University, the laboratories of which are open to students who give proof of their capacity to conduct original investigation. Graduates of other Universities who spend two years in the laboratory as Research Students are eligible for the D.Sc. degree of the University, and special chemicals and apparatus are provided free of charge. Graduate workers can also qualify for the Berry, 1851 Exhibition, and Carnegie Research Scholarships or Fellowships.

Students may work either independently or in collaboration with the Professor, to whom all communications should be addressed.

QUEEN'S UNIVERSITY, BELFAST.

Professor—E. A. Letts, Ph.D., D.Sc., F.R.U.I., &c.

Lecturer on Organic Chemistry—A. W. Stewart, D.Sc.

I.—*Chemistry.*—The lectures are delivered at 12 o'clock on the first five days of each week, and terminate about the end of March. The course embraces the elements of Physical, Inorganic, and Organic Chemistry. Fee, £3 3s.

II.—*Advanced Chemistry.*—Inorganic and Organic. The lectures are given at such days and hours as suit the convenience of the class. Fee, £2 2s.

III.—*Practical Chemistry.*—In this course the Students are instructed in the general methods of Qualitative and Quantitative Analysis, Inorganic preparations, &c. The class is held on four days in the week during the second term for two hours each day. Fee, £3 3s.

IV.—*Practical Chemistry for Engineering Students.*—A special course is given during the third term. Fee, £3 3s.

V.—*Laboratory Pupils.*—The Chemical Laboratories are open from the second week in October to the beginning of July, on the first five days of the week, from 10 a.m. —5 p.m. (except during the vacations). Students are admitted as working pupils on payment of a fee of £3 3s. for one term, £5 5s. for two, or £7 7s. for the whole Session. Facilities are provided for Students who wish to undertake research work.

Scholarships.—The following College Scholarships are awarded specially in connection with the schools of Chemistry and Physics:—Post Graduate Scholarships in Chemistry alone awarded annually of £50, and tenable for one year. Andrews Studentship in Chemistry and Physics, value about £80 annually, and tenable for two years. 1851 Exhibition Scholarships: One of these Scholarships has hitherto been placed at the disposal of the College every two years, of the annual value of £150, tenable for two or under special conditions for three years.

UNIVERSITY COLLEGE, CORK.

A CONSTITUENT COLLEGE OF THE NATIONAL UNIVERSITY OF IRELAND.

Professor—Augustus Edward Dixon, M.D.
Assistant Lecturer—John Taylor, M.Sc.
Demonstrator—James L. McKee, B.A., Ph.D.

The College Session will commence in October, 1913, and end in June, 1914. All classes are open to male and female students.

The following courses are provided:—

1. First Year Course for B.Sc.—General and Elementary Physical Chemistry, Inorganic Chemistry, Introductory Organic Chemistry, Practical Chemistry.
2. Second Year Course for B.Sc.—Advanced Inorganic Chemistry, Advanced Organic Chemistry, Practical Chemistry.
3. Third Year Course for B.Sc.—Physical Chemistry, Advanced Organic Chemistry, Practical Chemistry.
4. Courses in Systematic and in Practical Chemistry for students of Medicine proceeding to the Degrees of the University, or to the Examinations of the Medical Licensing Bodies of Dublin and of Edinburgh.
5. Courses in Systematic and in Practical Chemistry for Students of Engineering.
6. Laboratory Practical Course for the Diploma in Public Health.

Full particulars as to Lectures, Fees, Scholarships, Exhibitions, &c., are contained in the Regulations extracted from the College Calendar, which will be supplied on application to the Registrar.

NATIONAL UNIVERSITY OF IRELAND.

UNIVERSITY COLLEGE, GALWAY.

Professor—Alfred Senier, Ph.D., M.D., D.Sc., F.I.C., F.C.S., M.R.I.A.

Demonstrators—Robert B. Forster, Ph.D., and Miss R. Clarke, B.A.

The Session commences in September and ends in June.

Faculty of Science.—1. *First Year's Courses.*—Laboratory: Inorganic preparations, simple gravimetric quantitative and simple qualitative determinations. Lectures: A study of the chief non-metallic elements, their reactions and compounds, the molecular and atomic hypotheses, the leading metals, and an elementary consideration of the constitution and reactions of typical fatty and aromatic organic compounds. 2. *Second Year's Courses.*—Laboratory: Organic preparations, complex qualitative and quantitative inorganic determinations. Lectures: Advanced inorganic and organic chemistry. 3. *Third Year's Courses*—Laboratory: Qualitative and quantitative organic determinations, molecular weight determinations, gas analysis, thermo-electro and photo-chemical and other physical determinations. Lectures: General, physical, inorganic, and organic chemistry, a detailed study of special branches, and the historical development of chemistry.

Faculty of Arts.—*First Year's Course.*—Same as Faculty of Science.

Faculty of Medicine.—*First Year's Courses.*—Laboratory: Same as in Faculty of Science, but less detailed, and including the detection of the chief alkaloids, glucosides, and carbohydrates, and the chemical examination of urine. Lectures: Same as in Faculty of Science, first year.

Faculty of Engineering.—*First Year's Courses.*—Laboratory: Same as in Faculty of Science, but less detailed, and including a special study of metals, alloys, and other materials used in building construction, also determination of hardness in waters. Lectures: Same as in the Faculty of Science, first year.

The College offers a Scholarship in Chemistry for competition in alternate years of the value of £60, and Chemistry enters into the subjects required for numerous Scholarships in the Faculties of Science, Medicine, and Engineering. The Royal Commissioners for the Exhibition of 1851 offer every two years a Science Research Scholarship of £150 per annum. This Scholarship has already been held by six Chemistry Students of this College.

For details as to Fees, Regulations as to Scholarships, and other particulars apply to the Registrar, from whom the Calendar and other College publications may be obtained.

ROYAL COLLEGE OF SCIENCE, DUBLIN.

The Royal College of Science supplies, as far as practicable, a complete course of instruction in Science applicable to the Industrial Arts, and is intended also to aid in the instruction of teachers for the local Schools of Science.

Diplomas are awarded in the Faculties of Engineering (Mechanical and Electrical), Applied Chemistry, and Agriculture. If accompanied by a certificate from the Professor of Chemistry, the Diploma of Associate of the Royal College of Science in the Faculty of Applied Chemistry is recognised by the Council of the Institute of Chemistry of Great Britain and Ireland as qualifying candidates for admission to the practical examinations of the Institute.

The instruction in Chemical Science includes (1) General Inorganic Chemistry, Elementary and Advanced; (2) Organic Chemistry, Elementary and Advanced; (3) Analytical and Experimental Chemistry; (4) Physical Chemistry; (5) Metallurgical and Technological Chemistry and Assaying; (6) Instruction in Chemical Research.

Fees payable by Non-Associate Students:—£2 for each separate Course of Lectures. For Analytical Chemistry and Research—£5 for three months; £9 for six months; £12 for the entire session. Assaying—£5 for three months; £9 for six months. £12 for the entire session.

There are four Royal Scholarships of the value of £50 each yearly, with Free Education, including Laboratory Instruction, tenable for two years; two become vacant each year; they are awarded on the results of their examinations to Associate Students, not being Royal Exhibitioners, who have been a year in the College.

A limited number of Scholarships in Science and Technology are competed for each year. These Scholarships are of the value of £50 a year for four years, and, in addition, entitle the holder to free instruction during the full Associateship Course.

For further particulars apply to the Registrar.

PROFESSIONAL CHEMICAL QUALIFICATION

(F.I.C. AND A.I.C.).

THE INSTITUTE OF CHEMISTRY OF GREAT BRITAIN AND IRELAND.—The Institute of Chemistry was founded in October, 1877, and incorporated by Royal Charter in June, 1885, to elevate the profession of Chemistry, by setting up a high standard of scientific and practical proficiency for persons desirous of becoming professional consulting and technological chemists, public analysts, and chemical advisers, by examining Candidates, and granting certificates of competency, and by insisting on the observance of strict rules in regard to professional conduct. *The Studentship.*—Every Candidate for admission to the Studentship is required to produce evidence that he is at least seventeen years of age, and that he has passed a Preliminary Examination in subjects of general education, recognised by the Council of the Institute. He must also show that, at the time of making application for registration, he is working at a College or University recognised by the Council, or under the direction of a Fellow of the Institute in an approved laboratory. *The Intermediate Examination in General Theoretical and Practical Chemistry.*—Candidates for admission to the Intermediate Examination (Fee, £5 5s.) are required to produce evidence (I.) of having passed an approved Preliminary Examination in subjects of general education; (II.) of having regularly attended systematic day courses, in a College or University recognised by the Council, during at least three academic years, in theoretical and practical Chemistry, and courses in Physics, Elementary Mathematics, and one of the following subjects, in accordance

with the Regulations of the Institute: (i.) Higher Physics; (ii.) Advanced Mathematics; (iii.) Mechanics and Chemical Engineering; (iv.) Metallurgy; (v.) Geology and Mineralogy; (vi.) Physiology; (vii.) Bacteriology; (viii.) Agriculture; (ix.) Elementary Botany; (x.) Elementary Biology; and (III.) of having satisfactorily passed the Class Examinations in all the subjects required to be taken. As an alternative in the matter of training (II.), a candidate may take two years' day courses in a recognised Institution as indicated above, and work systematically for two other years under a Fellow of the Institute in an approved laboratory. A Candidate who has taken a Degree in Science (including Inorganic and Organic Chemistry, and Physics in the Degree Examination, Mathematics having been also taken at either the Final or Intermediate University Examination) in a University recognised by the Council, is eligible for admission to the Intermediate Examination of the Institute. Holders of certain Honours Degrees or Diplomas are exempt from passing the Intermediate, and, by virtue of their qualifications, are eligible for admission to the Final Examination direct. A Candidate who has passed the Intermediate Examination of the Institute, or who is entitled to claim exemption from passing the Intermediate Examination, is eligible for admission to the Final Examination. *The Final Examination* (Fee, £5 5s.) *for the Associateship (A.I.C.).*—This comprises, in addition to a general knowledge of all branches of chemistry, a thorough knowledge of one branch—Mineral chemistry; metallurgical chemistry; physical chemistry; organic chemistry; chemistry (including microscopy) of food and drugs, fertilisers and feeding-stuffs, soils, and water; or biological chemistry. All Candidates for the Final Examination are required to translate French and German technological literature, with the aid of dictionaries. Candidates taking the food and drugs section must take a course in botany, and those taking biological chemistry a course in biology. *Fellowship (F.I.C.).*—For admission to the Fellowship, an Associate is required to have been registered for three years, and to have been continuously engaged during that period in the study and practical work of applied chemistry in a manner satisfactory to the Council.

Full particulars are given in "The Book of Regulations for the Admission of Students, Associates, and Fellows," which may be obtained (gratis) from the Registrar, 30, Bloomsbury Square, London, W.C. Past Examination Papers, Annual Sets, 6d. each.

CHEMICAL LECTURES, CLASSES, AND LABORATORY INSTRUCTION.

City and Guilds of London Institute—The operations of the Institute are divided broadly into four branches:—(1) The City and Guilds (Engineering) College, (2) the City and Guilds Technical College, Finsbury, (3) the City and Guilds South London Technical Art School, and (4) the Department of Technology of the Institute. Programmes of the London Colleges may be had on application to the Temporary Offices during the rebuilding of Gresham College, Leonard Street, E.C., or from the respective Colleges. The Technological Examinations (Examinations Department, Exhibition Road, S.W.), are conducted once every year at various centres throughout the kingdom. The Programme of the College, containing full particulars of the conditions of entrance, fees, and courses of instruction, may be had on application. *City and Guilds (Engineering) College, Exhibition Road.*—The object of this Institution is to give to London a College for the higher technical education, in which advanced instruction shall be provided in those kinds of knowledge which bear upon the different branches of productive industry, whether Manufactures or Arts. The main purpose of the instruction given is to practically demonstrate the application of different branches of science to various manufacturing industries. In order that this instruction may be efficiently carried out, the Institution, in addition to the lecture theatres and class rooms, is fitted with laboratories, drawing offices, and workshops; and opportunities are afforded for the prosecution of original research, with the object of the more thorough training of the students, and for the elucidation of the theory of industrial processes. The courses of instruction are arranged to suit the requirements of—1. Persons training to become Technical Teachers; 2. Persons preparing to enter Engineers' or Architects' offices, or Manufacturing works; 3. Persons who desire to acquaint themselves with the scientific principles underlying the particular branch of industry in which they are engaged. *City and Guilds Technical College, Finsbury.*—Professor of Chemistry, Raphael Meldola, F.R.S. The operations of the Technical College, Finsbury, are divided into two distinct portions: Day Classes for those who are able to devote one, two, or three years to systematic technical education; Evening Classes for those who are engaged in industrial or commercial occupations in the daytime and who desire to receive supplementary instruction in the application of Science and of Art to the trades and manufactures in which they are concerned or employed. Each Professor is assisted by Demonstrators. Besides these there are Lecturers and Teachers in the various special subjects. *South London Technical Art School.*—Classes in Modelling, Design, Drawing and Painting.

City of London College, White Street, Moorfields.—I. S. Scarf, F.I.C., F.C.S., and Assistants. Classes and Laboratory Practice in Chemistry, Botany, and Geology, open to Students of both sexes. Day Commercial School.

Battersea Polytechnic.—Principal, S. G. Rawson, D.Sc., F.I.C. Inorganic, Organic, and Technological Chemistry, John Wilson, M.Sc. (Vict.), F.I.C., and Assistants. Complete courses of Instruction are given in Chemistry (Inorganic and Organic), together with Physics, Electricity, Engineering subjects, Bacteriology, Materia Medica, Paper Making and Testing, Oils and Fats, Dyeing, &c., for intending technological and works chemists. Certain of the Courses (Day and Evening) are recognised by the University of London in preparation for the B.Sc., for which examination (Pass and Honours) complete courses of instruction, under recognised teachers, are provided. Special Evening Courses in various Technical subjects. (For further information see College Calendar).

Borough Polytechnic Institute, 103, Borough Road, S.E.—Chemistry Department under the Direction of C. Dorée, M.A., D.Sc. Evening Lectures and Laboratory Work in Inorganic and Organic Chemistry. Special Lectures and Laboratory Courses in Electro chemistry and Electro-chemical Analysis. Special Courses of Lectures on various Technical subjects. (For further information see College Calendar).

Birkbeck College, Breams Buildings, Chancery Lane.—Chemistry Courses conducted by Dr. Alex. McKenzie prepare for various Examinations, the B.Sc. and M.B. Degrees of the London University, Conjoint Board, Pharmaceutical Examinations, Board of Education, &c. The Session will commence on Monday, Sept. 29. The Day and Evening courses of study include Chemistry, Physics, Botany, Zoology, Geology, Mathematics, Latin, Greek, Modern Languages, Economics, Geography, Logic, History, and various branches of Law. All the Courses are conducted by recognised teachers of the University and provide for the Examinations of the University of London. The Calendar supplies detailed information respecting the Courses of Study, Examinations, &c.

Northern Polytechnic Institute, Holloway Road, N.—Principal, R. S. Clay, D.Sc. Instruction in theoretical and practical Inorganic and Organic Chemistry. Systematic Day and Evening Courses for the London University Degrees, Pass and Honours, also for the Board of

Education examinations. Prospectus sent free on application to the Secretary.

Northampton Polytechnic Institute, St. John Street, E.C.—Principal, R. Mullineux Walmsley, D.Sc., &c. Classes in Electro-chemistry, Electro-plating, Electro-metallurgy, Electrotyping, Stereotyping, and Metal Colouring. (For full details see Prospectus).

South Western Polytechnic Institute, Chelsea.—Principal, Sidney Skinner, M.A. Head of the Chemical Department, J. B. Coleman, A.R.C.S., F.I.C. Day and Evening Courses in Theoretical and Practical Chemistry and several branches of Applied Chemistry including Metallurgy, Assaying, Photography, &c. Systematic Courses are held for the Matriculation, Inter. Sci., and B.Sc. Examinations (Pass and Honours) of the University of London. The Day Course in Chemistry is of four years' duration; it gives a thorough training to those who wish to become Consulting or Industrial Chemists. Prospectus of Day and Evening Classes may be obtained from the Secretary, 1d., by post 3½d.

East London College, Mile End Road, E.—Chemistry: Professor, J. T. Hewitt, M.A., D.Sc., Ph.D., F.R.S. Lectures and Practical Classes are held, the regular College Course being three years. The work of the first year corresponds with the requirements of the Int. Sci., Lond., that of the next two years with the degree examination, B.Sc. (Honours and Pass). Special attention is given to Research and Post-graduate studies. Evening Classes for London University Degrees are also held.

Sir John Cass Technical Institute, Jewry Street, Aldgate.—Principal, Charles A. Keane, D.Sc., Ph.D., &c., assisted by R. S. Willows, M.A., D.Sc., H. Burrows, A.R.C.S., Ph.D., F.I.C., G. F. Morrell, B.Sc., Ph.D., &c., G. Senter, D.Sc., &c., Arthur R. Ling, F.I.C., C. O. Bannister, A.R.S.M., M.I.M.M., G. Patchin, A.R.S.M., Wesley J. Lambert, Assoc.Inst.C.E., Arthur Harden, D.Sc., F.R.S., &c., J. S. S. Brame, E. C. Snow, M.A., D.Sc., F. J. Harlow, B.Sc., &c. The new Session of the Sir John Cass Technical Institute, which is specially devoted to technical training in Experimental Science and in the Artistic Crafts, will commence on Monday, September 22nd. The instruction in experimental Science provides systematic courses in Mathematics, Physics, and Chemistry for London University examinations in addition to the courses on higher technological instruction, which form a special feature of the work of the Institute. In connection with the latter, several new departures are being made for the coming Session. The curriculum in connection with the Fermentation Industries has been much developed, and now includes courses of instruction on Brewing and Malting, Bottling and Cellar Management, Brewery Plant, and on the Micro-biology of the Fermentation Industries. A connected series of lectures dealing with the Supply and Control of Power has also been arranged to meet the requirements of those engaged in works connected with Chemical, Electrical, and the Fermentation Industries. These will comprise a course of 20 lectures on the Supply and Control of Liquid, Gaseous, and Solid Fuel, a course of 5 lectures on Electrical Supply and Control, and a connected course of 5 lectures on the Transmission of Power. In the department of Physics and Mathematics, a special course of Lectures and Demonstrations will be given on Colloids, which will deal with the methods employed in their investigation and their relation to technical problems; also special courses of Lectures on the Methods of Differential and Integral Calculus, and on the Theory and Application of Mathematical Statistics, the latter of which will treat of the application and modern mathematical methods of dealing with statistical data in social, educational, economic, and physical problems. Opportunity will be given to students to investigate problems on their own account. In the Metallurgy department, in addition to the ordinary courses of instruction in general Metallurgy, special courses of an advanced character are provided on Gold, Silver, and allied metals, on Iron and Steel, on Metallography and Pyrometry, on Metals used in the Motor Car Industry, on Mining, Mine Surveying, and on Mineralogy.

University Tutorial College, 32, Red Lion Square, Holborn, W.C.—This Institution contains large Laboratories for Chemistry, Physics, Biology, Geology, and other subjects. Classes are specialised for Examinations of London University, but students may take up work for any Examination. The special feature of the College is that work goes on all the year round, thus affording students residing in the Country an opportunity of doing practical work during their Vacations.

East Ham Technical College.—Principal, W. H. Barker, B.Sc. Head of Chemical Department—A. E. Dunstan, D.Sc. (Lond.). Lecturers—F. B. Thole, B.Sc.; E. D. Griffiths, B.Sc.; R. W. Wilson, F.C.S. Demonstrators—S. J. Plaice; A. G. Mussell. Chemical Engineering and Gas Engineering—A. J. Nice. Gas Supply—G. Jenkins. Soap Manufacture, and Oils, Fats, and Waxes—A. J. Harvey. Tar Distillation, &c.—A. J. Nice, and A. E. Dunstan, D.Sc. Metallurgy—F. B. Thole, B.Sc. Sugar Manufacture—A. Wade. Evening Classes and Secondary School.

Blackburn Municipal Technical School.—Chemistry: Robert H. Pickard, D.Sc.(Lond.), &c., assisted by Jos. Yates, M.Sc., F.I.C., Jos. Kenyon, B.Sc., F.I.C., and W. Lewcock, B.Sc. Session opened Monday, Sept. 22. Full details of the Classes are given in the "Students' Handbook," which may be had at the Institution (price 1d., by post 3d.).

Redruth School of Mines (now incorporated in the School of Metalliferous Mining, Cornwall).—Complete courses of Practical and Theoretical instruction are given in Inorganic Chemistry, Assaying, Mineralogy, Blowpipe Analysis, Mine Surveying, Geology, Principles of Mining, Ore Dressing, Mechanical Engineering, &c., for intending Assayers, Mineral Chemists, Mining Engineers, and Surveyors. Practical instruction in Mining given at the Basset Mines, Ltd. Syllabus on application.

Municipal School of Technology, Sackville Street, Manchester.—Laboratories and workshops for Mechanical, Electrical, Sanitary and Hydraulic Engineering, Textile industries, Photography, Collotype and Photo-mechanical processes, Letterpress and Lithographic industries, and industries within the scope of Architecture. The provision for the teaching of Chemistry, as might be expected in a district where the Chemical industries are important, is of an exceptionally complete character. It comprises laboratories for Metallurgy, Brewing, Bleaching, Dyeing and Printing, Paper-making, and Electro-chemistry. The Bleaching, Dyeing, Printing and Finishing, and the Paper-making industries are in addition extensively equipped in a separate building with machinery and appliances on an industrial scale. A Brew-house is also equipped on the low gravity principle, with a plant of four bushel capacity.

Wolverhampton Municipal Science and Technical School.—Principal, J. D. Coales, D.Sc., M.I.E.E.; Inorganic and Organic Chemistry, Th. J. Murray, M.Sc., Ph.D.; Physics, A. T. Harrison, B.Sc.; Botany, Sidney Phillips, Ph.C. Human Physiology and Hygiene, H. J. Tench, A.R.S.I. Materia Medica and Pharmacy, F. W. Thompson, Ph.C. Day Classes in Chemistry, and Evening Classes in Chemistry, Physics, Botany, French, &c. Special arrangements are made for the requirements of Pharmaceutical and Medical Students and Chemical Trades. Session commences Monday, Sept. 15th. For other particulars and programme, apply G. F. Chell, Secretary.

Municipal Technical Institute, Belfast.—Principal, F. C. Forth, A.R.C.Sc.I. Chemistry, Prof. H. Wren, M.A., Ph.D., D.Sc., and Assistants. Day and Evening Courses. Session opened Sept. 1st.

THE SCIENTIFIC WEEK.

(From Our Own Paris Correspondent).

NEW PROCESS FOR THE VULCANISATION OF RUBBER.

In trying to apply practically the fine studies of M. Victor Henri (Assistant in Dr. Dastre's Laboratory of Physiology in the Sorbonne) on the depolymerising action of ultra-violet rays on indiarubber, M. G. Bornstein has just made a curious discovery—*these radiations can vulcanise rubber.*

It is known that, industrially, amongst other ingredients sulphur is mixed with pure rubber by a final heating in an autoclave. This sulphur is combined with the rubber, which is henceforth rendered capable of thoroughly resisting the variations of temperature. Now, in preparing very thin fine pellicles with virgin rubber and a little sulphur, in order to obtain the fixation of the sulphur, that is to say, the vulcanisation, it suffices to enlighten the mixture with ultra-violet radiations.

It remains to be seen if the fact will have any consequence applicable to industry. The fact is, it does not appear that the new method can be substituted for the classical process of vulcanisation; but it would be rash to come to a too decided conclusion; and even if it remains in the theoretical domain, the fact is nevertheless interesting.

INTERPLANETARY VOYAGES.

M. Esnault Pelteric, the well-known constructor of aeroplanes, has just made a whole series of calculations in order to solve the problem of interplanetary voyages. Actually it appears difficult that flying-machines will exceed a speed of more than 200 kilometres an hour. It would thus take 200 hours, or a little more than eight days, to go round the world. To escape from the attraction of the earth M. Esnault Pelteric has calculated that it would be necessary to endow the projectile that was to leave the earth with a speed of 11 kilometres per second.

The new interplanetary apparatus would no longer seem to be the aeroplane, but a cannon ball, similar to that which Jules Verne imagined in his famous novel "From the Earth to the Moon." This shell would be propelled by rockets having the property of uninterrupted continuity. At a speed of 11 kilometres per second a machine of this kind would go round the world in sixty-six minutes, and from Paris to Nice in less than two minutes. This prodigious speed could be obtained by the disintegration of some kilogrms. of radium. One of these projectiles provided with 27 kilogrms. of radium could make the voyage from the earth to the moon in less than forty-nine hours. It is true that the radium would have to give out all the formidable energy it contains in forty-nine hours, whereas in the actual state of science it would require 2800 years to arrive at the same result. With 400 kilogrms. of radium on board it would be possible to go as far as the planet Venus. But all these calculations are but the sport of statisticians.

AN EXPLANATION OF CERTAIN EARTHQUAKES.

M. Barrois has just read at the Academy of Medicine a memoir of Dr. de Montessus de Ballore on a cause that may be assigned for certain earthquakes. The earthquake that took place on August 9th, 1912, in the neighbourhood of Galipoli in Turkey, was studied on the spot by M. Macovei, who has specially described the geology of the lengthened epicentral region parallel to the sea of Marmora, between Rodosto and Gallipoli. Along the length of 20 kilometres of this axis there exists an overlapping of the Sarmatian on to the Miocene strata. In may then be inferred that a tertonic line of this importance must have a relation of cause to effect with the earthquake.

THE RISKS OF PHOTOGRAPHERS.

The professional risks of photographers are many, and sometimes very serious. They sometimes affect their cutaneous covering, their blood, and their viscera. The first kind of affection has been known for a long time. In perpetual contact with liquids of variable chemical composition the skin of their hands is exposed to eruptions of various intensity, but generally of an eczematous nature. This, after all, is not special only to photographers. The disorders of the blood, too special in their essence for us to enter into all their details, would, according to M. Agasse Lafont, have two distinct causes; on the one hand, there would be a chronic intoxication caused by the salts of silver, the consequences of which recal those brought on by mercurial poisoning; on the other hand, with perforators of cinematographic films that are a little on the margin of the photographic industry, what is specially to be rendered responsible are the vapours of acetate, of amylic acid, and of acetone, which appear to cause globular lesions resembling those caused by intoxication by benzene. Lastly, M. Thiry, after analysing a work of Lenenberger, who establishes the frequency of malignant tumours in the manufacture of aniline colours, shows that the guilty in this matter might certainly be certain groups of chemical substances to which belong paramidophenol and metol. Consequently there is a possible danger of the same nature for photographers who frequently use chemical bodies of this kind. Although this conclusion may appear pessimist and hasty, it is well to follow the counsel of M. Thiry, who considers that the preservation from these accidents lies in a particularly strict regard to hygiene in photographic work. Special garments for the workshop, careful and frequent washing of hands, ventilation and cleanliness of the workshops and photographic studios, as well as the respiratory mask, useful in certain fabrications, all of which precautions will appear but slightly troublesome when compared with the serious complaints and troubles whose arrival may be thus prevented.

THE F-RAYS DO NOT EXIST.

The discovery that was announced of a new series of rays, the F-rays, has just been contradicted. According to very precise and detailed information published by the *Eclair*, it appears that the results obtained are not at all conclusive. The F-rays appear to be an illusion similar to that of which the scientific world was a victim when the physicist Blondlot, Professor at the Faculty of Nancy, professed to have discovered the N rays.

NOTICES OF BOOKS.

Preliminary Chemistry. By H. W. BAUSOR, M.A. London: University Tutorial Press, Ltd. 1913.

THIS book contains a short course of practical and theoretical chemistry which covers the syllabus of the Cambridge Preliminary Local Examination. Easy experiments on the nature and composition of air, water, chalk, and salt, and on the properties and simpler compounds of sulphur and carbon are described in such a way that the student should usually be able to perform them with very little help or supervision from the teacher, and the author endeavours by the text to give the student definite knowledge of the facts and principles of chemistry, as well as to train his powers of observation and inference. Each chapter is well summarised, and questions and additional practical exercises are given.

Literatur-Register der Organischen Chemie. ("Register of the Literature of Organic Chemistry"). Edited by R. STELZNER. Vol. I. *The Literature of the Years* 1910 *and* 1911. Braunschweig: Friedrich Vieweg und Sohn. 1913. (M. 84).

THIS admirable dictionary of organic compounds follows Richter's system of tabulation, and will be found indispensable by all who are interested in organic research. The compounds of carbon are arranged in order of increasing complexity, and under each empirical formula

references are given to the literature relating to all the compounds having that formula. 22,000 different substances are included in this volume, which covers the years 1910 and 1911. In addition to the references to the literature of each substance, very brief notes are given as to the contents of the papers, &c., quoted, so that some account of the occurrence, properties, and transformations of every substance is to be found in the book.

MISCELLANEOUS.

Tests for Coal-tar Colours in Aniline Lakes.—Messrs. Charles Griffin and Co. have in their list an important and valuable work bearing this title, by George Zerr, translated by Dr. C. Mayer, of Burgdorf. The complex nature of synthetical dyes renders their analysis no easy matter, and the present work should prove exceedingly helpful to workers in this field. Until the advent of this work there was practically no literature on the subject. This volume provides all that is needed, and should be in every laboratory dealing with coal-tar colours.

The Chemical Laboratory Fresenius at Wiesbaden, Germany.—During the Summer Term, 1913, the Chemical Laboratory Fresenius was attended by thirty-six students, including three ladies. Of these twenty-one were from Germany, six from Russia, two from Luxemburg, one from Austria, one from Denmark, one from England, one from France, one from Holland, one from Sweden, and one from Brazil. The Directors of the Institute, Geh. Regierungsrat Prof. Dr. H. Fresenius and Prof. Dr. W. Fresenius, are assisted by four duly qualified teachers and heads of departments. Besides these there is a staff of thirty-two assistant chemists, including six ladies. The next Winter Term will commence on October 15th. During the Summer Term, 1913, a number of scientific treatises originated from the Laboratory Fresenius; they were published in different chemical journals. As special prints appeared: — "Chemische und physikalisch-chemische Untersuchung der Solquelle zu Liesborn bei Lippstadt i.W., sowie Untersuchung derselben auf Radioaktivität von. Geh. Regierungsrat Prof. Dr. H. Fresenius; Wiesbaden, C. W. Kreidel's Verlag, 1913." "Chemische Untersuchung der Herzogsquelle (Slavonski Evian) zu Orahovica in Slavonien von Geh. Regierungsrat Prof. Dr. H. Fresenius; Wiesbaden, C. W. Kreidel's Verlag, 1913." "Chemische und physikalisch-chemische Untersuchung des Luitpoldsprudels zu Bad Kissingen nebst Untersuchungen über dessen Radioaktivität von Dr. R. Fresenius and Dr. L. Grünhut; Wiesbaden, C. W. Kreidel's Verlag, 1913." Besides the scientific work a great number of chemical analyses were executed during the summer half year, 1913, for commercial, mining, industrial, and agricultural purposes, also in the interest of Sanitary-boards, Criminal and other State Departments.

The Apprenticeship and Skilled Employment Association notifies that it can recommend for work in commercial and other laboratories several promising lads who have been acting as laboratory monitors or assistants in London County Council Higher Grade or Secondary Schools, and whose services the Council are unable to retain after they have reached the age of 17. The Association has already placed some lads in suitable occupations in which they are doing well, and has now had a fresh batch referred to it. Further information may be obtained from the Association, the offices of which are 61, Denison House, Vauxhall Bridge Road, S.W.

THE CHEMICAL NEWS.

VOL. CVIII., No. 2807.

BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

BIRMINGHAM, 1913.

INAUGURAL ADDRESS OF THE PRESIDENT,

Sir OLIVER LODGE, D.Sc., LL.D., F.R.S., &c.

CONTINUITY.

Natura non vincitur nisi parendo.

FIRST let me lament the catastrophe which has led to my occupying the Chair here in this City. Sir William White was a personal friend of many here present, and I would that the citizens of Birmingham could have become acquainted with his attractive personality, and heard at first hand of the strenuous work which he accomplished in carrying out the behests of the Empire in the construction of its first line of defence.

Although a British Association Address is hardly an annual stocktaking, it would be improper to begin this year of Office without referring to three more of our losses:—One that cultured gentleman, amateur of science in the best sense, who was chosen to preside over our Jubilee meeting at York thirty-two years ago. Sir John Lubbock, first Baron Avebury, cultivated science in a spirit of pure enjoyment, treating it almost as one of the Arts; and he devoted social and political energy to the welfare of the multitude of his fellows less fortunately situated than himself.

Through the untimely death of Sir George Darwin the world has lost a mathematical astronomer whose work on the Tides and allied phenomena is a monument of power and achievement. So recently as our visit to South Africa he occupied the Presidential Chair.

By the third of our major losses, I mean the death of that brilliant mathematician of a neighbouring nation who took so comprehensive and philosophic a grasp of the intricacies of physics, and whose eloquent though sceptical exposition of our laws and processes, and of the modifications entailed in them by recent advances, will be sure to attract still more widespread attention among all to whom the rather abstruse subject-matter is sufficiently familiar. I cannot say that I find myself in agreement with all that Henri Poincaré wrote or spoke in the domain of physics, but no physicist can help being interested in his mode of presentation, and I may have occasion to refer, in passing, to some of the topics with which he dealt.

And now, eliminating from our purview, as is always necessary, a great mass of human activity, and limiting ourselves to a scrutiny on the side of pure science alone, let us ask what, in the main, is the characteristic of the promising though perturbing period in which we live. Different persons would give different answers, but the answer I venture to give is—Rapid progress, combined with Fundamental scepticism.

Rapid progress was not characteristic of the latter half of the nineteenth century—at least not in physics. Fine solid dynamical foundations were aid, and the edifice of knowledge was consolidated; but wholly fresh ground was not being opened up, and totally new buildings were not expected.

> "In many cases the student was led o believe that the main facts of nature were all known, that the chances of any great discovery being made by experiment were vanishingly small, and that therefore the experimentalist's work consisted in deciding between rival theories, or in finding some small residual effect, which might add a more or less important detail to the theory."—*Schuster.*

With the realisation of predicted ether waves in 1888, the discovery of X-rays in 1895, spontaneous radio-activity in 1896, and the isolation of the electron in 1898, expectation of further achievement became vivid; and novelties, experimental, theoretical, and speculative, have been showered upon us ever since this century began. That is why I speak of rapid progress.

Of the progress I shall say little—there must always be some uncertainty as to which particular achievement permanently contributes to it; but I will speak about the fundamental scepticism.

Let me hasten to explain that I do not mean the well-worn and almost antique theme of Theological scepticism; that controversy is practically in abeyance just now. At any rate the major conflict is suspended; the forts behind which the enemy has retreated do not invite attack; the territory now occupied by him is little more than his legitimate province. It is the scientific allies, now, who are waging a more or less invigorating conflict among themselves; with philosophers joining in. Meanwhile the ancient foe is biding his time and hoping that from the struggle something will emerge of benefit to himself. Some positions, he feels, were too hastily abandoned and may perhaps be retrieved; or, to put it without metaphor, it seems possible that a few of the things prematurely denied, because asserted on inconclusive evidence, may after all, in some form or other, have really happened. Thus the old theological bitterness is mitigated, and a temporising policy is either advocated or instinctively adopted.

To illustrate the nature of the fundamental scientific or philosophic controversies to which I do refer, would require almost as many addresses as there are Sections of the British Association, or at any rate as many as there are chief cities in Australia; and perhaps my successor in the Chair will continue the theme; but, to exhibit my meaning very briefly, I may cite the kind of dominating controversies now extant, employing as far as possible only a single word in each case so as to emphasise the necessary brevity and insufficiency of the reference.

In Physiology the conflict ranges round *Vitalism*. (My immediate predecessor dealt with the subject at Dundee).

In Chemistry the debate concerns *Atomic structure*. (My penultimate predecessor is well aware of pugnacity in that region).

In Biology the dispute is on the laws of *Inheritance*. (My successor is sure to deal with this subject; probably in a way not deficient in liveliness).

And besides these major controversies, debate is active in other sections.

In Education, *Curricula* generally are being overhauled or fundamentally criticised, and revolutionary ideas are promulgated concerning the advantages of freedom for infants.

In Economic and Political Science, or Sociology, what is there that is not under discussion? Not property alone, nor land alone, but everything—back to the garden of Eden and the inter-relations of men and women.

Lastly, in the vast group of Mathematical and Physical Sciences, "slurred over rather than summed up as Section A," present-day scepticism concerns what, if I had to express it in one word, I should call *Continuity*. The full meaning of this term will hardly be intelligible without explanation, and I shall discuss it presently.

Still more fundamental and deep-rooted than any of these sectional debates, however, a critical examination of scientific foundations generally is going on; and a kind

of philosophic scepticism is in the ascendant, resulting in a mistrust of purely intellectual processes and in a recognition of the limited scope of science.

For science is undoubtedly an affair of the intellect, it examines everything in the cold light of reason; and that is its strength. It is a commonplace to say that science must have no likes or dislikes, must aim only at truth; or as Bertrand Russell well puts it:—

"The kernel of the scientific outlook is the refusal to regard our own desires, tastes, and interests as affording a key to the understanding of the world."

This exclusive single-eyed attitude of science is its strength; but, if pressed beyond the positive region of usefulness into a field of dogmatic negation and philosophising, it becomes also its weakness. For the nature of man is a large thing, and intellect is only a part of it; a recent part too, which therefore necessarily, though not consciously, suffers from some of the defects of newness and crudity, and should refrain from imagining itself the whole—perhaps it is not even the best part—of human nature.

The fact is that some of the best things are, by abstraction, excluded from Science, though not from Literature and Poetry; hence perhaps an ancient mistrust or dislike of science, typified by the Promethean legend. Science is systematised and *metrical* knowledge, and in regions where measurement cannot be applied it has small scope; or, as Mr. Balfour said the other day at the opening of a new wing of the National Physical Laboratory—

"Science depends on measurement, and things not measurable are therefore excluded, or tend to be excluded, from its attention. But Life and Beauty and Happiness are not measurable." And then characteristically he adds:—"If there could be a unit of happiness, Politics might begin to be scientific."

Emotion and Intuition and Instinct are immensely older than science, and in a comprehensive survey of existence they cannot be ignored. Scientific men may rightly neglect them, in order to do their proper work, but philosophers cannot.

So Philosophers have begun to question some of the larger generalisations of science, and to ask whether in the effort to be universal and comprehensive we have not extended our laboratory inductions too far. The Conservation of Energy, for instance—is it always and everywhere valid; or may it under some conditions be disobeyed? It would seem as if the second law of Thermodynamics must be somewhere disobeyed—at least if the age of the Universe is both ways infinite—else the final consummation would have already arrived.

Not by philosophers only, but by scientific men also, ancient postulates are being pulled up by the roots. Physicists and Mathematicians are beginning to consider whether the long known and well-established laws of mechanics hold true everywhere and always, or whether the Newtonian scheme must be replaced by something more modern, something to which Newton's laws of motion are but an approximation.

Indeed a whole system of non-Newtonian Mechanics has been devised, having as its foundation the recently discovered changes which must occur in bodies moving at speeds nearly comparable with that of light. It turns out in fact that both Shape and Mass are functions of Velocity. As the speed increases the mass increases and the shape is distorted, though under ordinary conditions only to an infinitesimal extent.

So far I agree; I agree with the statement of fact; but I do not consider it so revolutionary as to overturn Newtonian mechanics. After all, a variation of Mass is familiar enough, and it would be a great mistake to say that Newton's second law breaks down merely because Mass is not constant. A raindrop is an example of variable mass; or the earth may be, by reason of meteoric dust; or the sun, by reason of radio-activity; or a locomotive, by reason of the emission of steam. In fact, variable masses are the commonest, for friction may abrade any moving body to a microscopic extent.

That Mass is constant is only an approximation. That Mass is equal to ratio of Force and Acceleration is a definition, and can be absolutely accurate. It holds perfectly even for an electron with a speed near that of light; and it is by means of Newton's second law that the variation of Mass with Velocity has been experimentally observed and compared with theory.

I urge that we remain with, or go back to, Newton. I see no reason against retaining all Newton's laws, discarding nothing; but supplementing them in the light of further knowledge.

Even the laws of Geometry have been overhauled, and Euclidean Geometry is seen to be but a special case of more fundamental generalisations. How far they apply to existing space, and how far Time is a reality or an illusion, and whether it can in any sense depend on the motion or the position of an observer; all these things in some form or other are discussed.

The Conservation of Matter also, that main-mast of nineteenth century chemistry, and the existence of the Ether of Space, that sheet-anchor of nineteenth century physics,—do they not sometimes seem to be going by the board?

Prof. Schuster, in his American lectures, commented on the modern receptive attitude as follows:—

"The state of plasticity and flux—a healthy state, in my opinion,—in which scientific thought of the present day adapts itself to almost any novelty, is illustrated by the complacency with which the most cherished tenets of our fathers are being abandoned. Though it was never an article of orthodox faith that chemical elements were immutable and would not some day be resolved into simpler constituents, yet the conservation of mass seemed to lie at the very foundation of the creation. But nowadays the student finds little to disturb him, perhaps too little, in the idea that mass changes with velocity, and he does not always realise the full meaning of the consequences which are involved."

This readiness to accept and incorporate new facts into the scheme of physics may have led to perhaps an undue amount of scientific scepticism, in order to right the balance.

But a still deeper variety of comprehensive scepticism exists, and it is argued that all our laws of nature, so laboriously ascertained and carefully formulated, are but conventions after all, not truths; that we have no faculty for ascertaining real truth, that our intelligence was not evolved for any such academic purpose; that all we can do is to express things in a form convenient for present purposes, and employ that mode of expression as a tentative and pragmatically useful explanation.

Even *explanation*, however, has been discarded as too ambitious by some men of science, who claim only the power to describe. They not only emphasise the *how* rather than the *why*,—as is in some sort inevitable, since explanations are never ultimate—but are satisfied with very abstract propositions, and regard mathematical equations as preferable to, because safer than, mechanical analogies or models.

"To use an acute and familiar expression of Gustav Kirchhoff, it is the object of science to *describe* natural phenomena, not to *explain* them. When we have expressed by an equation the correct relationship between different natural phenomena we have gone as far as we safely can, and if we go beyond we are entering on purely speculative ground."

But the modes of statement preferred by those who distrust our power of going correctly into detail are far from satisfactory. Professor Schuster describes and comments on them, thus:—

"Vagueness, which used to be recognised as our great enemy, is now being enshrined as an idol to be worshipped. We may never know what constitutes atoms, or what is the real structure of the ether; why trouble therefore, it is said, to find out more about them. Is it not safer, on the contrary, to confine ourselves to a general talk on entropy, luminiferous vectors, and undefined symbols expressing vaguely certain physical relationships? What really lies at the bottom of the great fascination which these new doctrines exert on the present generation is sheer cowardice, the fear of having its errors brought home to it." . . .

"I believe this doctrine to be fatal to a healthy development of science. Granting the impossibility of penetrating beyond the most superficial layers of observed phenomena, I would put the distinction between the two attitudes of mind in this way: One glorifies our ignorance, while the other accepts it as a regrettable necessity."

In further illustration of the modern sceptical attitude, I quote from Poincaré:—

"Principles are conventions and definitions in disguise. They are, however, deduced from experimental laws, and these laws have, so to speak, been erected into principles to which our mind attributes an absolute value." . . .

"The fundamental propositions of geometry, for instance Euclid's postulate, are only conventions, and it is quite as unreasonable to ask if they are true or false as to ask if the metric system is true or false. Only these conventions are convenient." . . .

"Whether the ether exists or not matters little,—let us leave that to the metaphysicians; what is essential for us is that everything happens as if it existed, and that this hypothesis is found to be suitable for the explanation of phenomena. After all, have we any other reason for believing in the existence of material objects? That, too, is only a convenient hypothesis."

As an antidote against over-pressing these utterances I quote from Sir J. Larmor's Preface:—

"There has been of late a growing trend of opinion, prompted in part by general philosophical views, in the direction that the theoretical constructions of physical science are largely factitious, that instead of presenting a valid image of the relations of things on which further progress can be based, they are still little better than a mirage." . . .

"The best method of abating this scepticism is to become acquainted with the real scope and modes of application of conceptions which, in the popular language of superficial exposition—and even in the unguarded and playful paradox of their authors, intended only for the instructed eye—often look bizarre enough."

One thing is very notable, that it is closer and more exact knowledge that has led to the kind of scientific scepticism now referred to; and that the simple laws on which we used to be working were thus simple and discoverable because the full complexity of existence was tempered to our ken by the roughness of our means of observation.

Kepler's laws are not accurately true, and if he had had before him all the data now available he could hardly have discovered them. A planet does not really move in an ellipse but in a kind of hypocycloid, and not accurately in that either.

So it is also with Boyle's law, and the other simple laws in Physical Chemistry. Even Van der Waals' generalisation of Boyle's law is only a further approximation.

In most parts of physics simplicity has sooner or later to give place to complexity: though certainly I urge that the simple laws were true, and are still true, as far as they go, their inaccuracy being only detected by further real discovery. The reason they are departed from becomes known to us; the law is not really disobeyed, but is modified through the action of a known additional cause. Hence it is all in the direction of progress.

It is only fair to quote Poincaré again, now that I am able in the main to agree with him—

"Take, for instance, the laws of reflection. Fresnel established them by a simple and attractive theory which experiment seemed to confirm. Subsequently, more accurate researches have shown that this verification was but approximate; traces of elliptic polarisation were detected everywhere. But it is owing to the first approximation that the cause of these anomalies was found, in the existence of a transition layer; and all the essentials of Fresnel's theory have remained. We cannot help reflecting that all these relations would never have been noted if there had been doubt in the first place as to the complexity of the objects they connect. Long ago it was said: If Tycho had had instruments ten times as precise, we would never have had a Kepler, or a Newton, or Astronomy. It is a misfortune for a science to be born too late, when the means of observation have become too perfect. That is what is happening at this moment with respect to physical chemistry; the founders are hampered in their general grasp by third and fourth decimal places; happily they are men of robust faith. As we get to know the properties of matter better we see that continuity reigns. . . . . It would be difficult to justify [the belief in continuity] by apodeictic reasoning, but without [it] all science would be impossible."

Here he touches on my own theme, *Continuity*; for, if we had to summarise the main trend of physical controversy at present, I feel inclined to urge that it largely turns on the question as to which way ultimate victory lies in the fight between Continuity and Discontinuity.

On the surface of nature at first we see discontinuity; objects detached and countable. Then we realise the air and other media, and so emphasise continuity and flowing quantities. Then we detect atoms and numerical properties, and discontinuity once more makes its appearance. Then we invent the ether and are impressed with continuity again. But this is not likely to be the end; and what the ultimate end will be, or whether there is an ultimate end, is a question difficult to answer.

The modern tendency is to emphasise the discontinuous or atomic character of everything. Matter has long been atomic, in the same sense as Anthropology is atomic; the unit of matter is the atom, as the unit of humanity is the individual. Whether men or women or children—they can be counted as so many "souls." And atoms of matter can be counted too.

Certainly however there is an illusion of continuity. We recognise it in the case of water. It appears to be a continuous medium, and yet it is certainly molecular. It is made continuous again, in a sense, by the ether postulated in its pores; for the ether is essentially continuous. Though Osborne Reynolds, it is true, invented a discontinuous or granular Ether, on the analogy of the sea shore. The sands of the sea, the hairs of the head, the descendants of a Patriarch, are typical instances of numerable, or rather of innumerable, things. The difficulty of enumerating them is not that there is nothing to count, but merely that the things to be counted are very numerous. So are the atoms in a drop of water,—they outnumber the drops in an Atlantic Ocean—and, during the briefest time of stating their number, fifty millions or so may have evaporated; but they are as easy to count as the grains of sand on a shore.

The process of counting is evidently a process applicable to discontinuities, *i.e.*, to things with natural units; you can count apples and coins, and days and years, and people and atoms. To apply number to a continuum you

must first cut it up into artificial units; and you are always left with incommensurable fractions. Thus only is it that you can deal numerically with such continuous phenomena as the warmth of a room, the speed of a bird, the pull of a rope, or the strength of a current.

But how, it may be asked, does discontinuity apply to number? The natural numbers, 1, 2, 3, etc., are discontinuous enough, but there are fractions to fill up the interstices; how do we know that they are not really connected by these fractions, and so made continuous again?

(By number I always mean commensurable number; incommensurables are not numbers: they are just what cannot be expressed in numbers. The square root of 2 is not a number, though it can be readily indicated by a length. Incommensurables are usual in physics and are frequent in geometry; the conceptions of geometry are essentially continuous. It is clear, as Poincaré says, that "if the points whose co-ordinates are commensurable were alone regarded as real, the in-circle of a square and the diagonal of the square would not intersect, since the co-ordinates of the points of intersection are incommensurable.")

I want to explain how commensurable fractions do not connect up numbers, nor remove their discontinuity in the least. The divisions on a foot rule, divided as closely as you please, represent commensurable fractions, but they represent none of the length. No matter how numerous they are, all the length lies between them; the divisions are mere partitions and have consumed none of it; nor do they connect up with each other, they are essentially discontinuous. The interspaces are infinitely more extensive than the barriers which partition them off from one another; they are like a row of compartments with infinitely thin walls. All the incommensurables lie in the interspaces; the compartments are full of them, and they are thus infinitely more numerous than the numerically expressible magnitudes. Take any point of the scale at random, that point will certainly lie in an interspace: it will not lie on a division, for the chances are infinity to 1 against it.

Accordingly incommensurable quantities are the rule in physics. Decimals do not in practice terminate or circulate, in other words vulgar fractions do not accidentally occur in any measurements, for this would mean infinite accuracy. We proceed to as many places of decimals as correspond to the order of accuracy aimed at.

Whenever, then, a commensurable number is really associated with any natural phenomenon, there is necessarily a noteworthy circumstance involved in the fact, and it means something quite definite and ultimately ascertainable. Every discontinuity that can be detected and counted is an addition to knowledge. It not only means the discovery of natural units instead of being dependent on artificial ones, but it throws light also on the nature of phenomena themselves.

For instance:—

The ratio between the velocity of light and the inverted square root of the product of the electric and magnetic constants was discovered by Clerk Maxwell to be 1; and a new volume of physics was by that discovery opened.

Dalton found that chemical combination occurred between quantities of different substances specified by certain whole or fractional numbers; and the atomic theory of matter sprang into substantial though at first infantile existence.

The hypothesis of Prout, which in some modified form seems likely to be substantiated, is that all atomic weights are commensurable numbers; in which case there must be a natural fundamental unit underlying, and in definite groups composing, the atoms of every form of matter.

The small number of degrees of freedom of a molecule, and the subdivision of its total energy into equal parts corresponding thereto, is a theme not indeed without difficulty but full of importance. It is responsible for the suggestion that energy too may be atomic!

Mendeleeff's series again, or the detection of a natural grouping of atomic weights in families of seven, is another example of the significance of number.

Electricity was found by Faraday to be numerically connected with quantity of matter; and the atom of electricity began its hesitating but now brilliant career.

Electricity itself—*i.e.*, electric charge—strangely enough has proved itself to be atomic. There is a natural unit of electric charge, as suspected by Faraday and Maxwell and named by Johnstone Stoney. Some of the electron's visible effects were studied by Crookes in a vacuum; and its weighing and measuring by J. J. Thomson were announced to the British Association Meeting at Dover in 1899,—a fitting prelude to the twentieth century.

An electron is the natural unit of negative electricity, and it may not be long before the natural unit of positive electricity is found too. But concerning the nature of the positive unit there is at present some division into opposite camps. One school prefers to regard the unit of positive electricity as a homogeneous sphere, the size of an atom, in which electrons revolve in simple harmonic orbits and constitute nearly the whole effective mass. Another school, while appreciative of the simplicity and ingenuity and beauty of the details of this conception, and the skill with which it has been worked out, yet thinks the evidence more in favour of a minute central positive nucleus, or nucleus-group, of practically atomic mass; with electrons, larger—*i.e.*, less concentrated—and therefore less massive than itself, revolving round it in astronomical orbits. While from yet another point of view it is insisted that positive and negative electrons can only differ skew-symmetrically, one being like the image of the other in a mirror, and that the mode in which they are grouped to form an atom remains for future discovery. But no one doubts that electricity is ultimately atomic.

Even magnetism has been suspected of being atomic, and its hypothetical unit has been named in advance the magneton: but I confess that here I have not been shaken out of the conservative view.

We may express all this as an invasion of number into unsuspected regions.

Biology may be said to be becoming atomic. It has long had natural units in the shape of cells and nuclei, and some discontinuity represented by body-boundaries and cell-walls; but now, in its laws of heredity as studied by Mendel, number and discontinuity are strikingly apparent among the reproductive cells, and the varieties of offspring admit of numerical specification and prediction to a surprising extent; while modification by continuous variation, which seemed to be of the essence of Darwinism, gives place to, or at least is accompanied by, mutation, with finite and considerable and in appearance discontinuous change.

So far from Nature not making jumps, it becomes doubtful if she does anything else. Her hitherto placid course, more closely examined, seems to look like a kind of steeplechase.

Yet undoubtedly Continuity is the backbone of evolution, as taught by all biologists,—no artificial boundaries or demarcations between species—a continuous chain of heredity from far below the amœba up to man. Actual continuity of undying germ-plasm, running through all generations, is taught likewise; though a strange discontinuity between this persistent element and its successive accessory body-plasms—a discontinuity which would convert individual organisms into mere temporary accretions or excretions, with no power of influencing or conveying experience to their generating cells—is advocated by one school.

Discontinuity does not fail to exercise fascination even in pure Mathematics. Curves are invented which have no tangent or differential coefficient, curves which consist of a succession of dots or of twists; and the theory of commensurable numbers seems to be exerting a dominance over philosophic mathematical thought as well as over physical problems.

And not only these fairly accepted results are prominent, but some more difficult and unexpected theses in the same direction are being propounded, and the atomic character of Energy is advocated. We had hoped to be honoured by the presence of Professor Planck, whose theory of the *quantum*, or indivisible unit or atom of energy, excites the greatest interest, and by some is thought to hold the field.

Then, again, Radiation is showing signs of becoming atomic or discontinuous. The corpuscular theory of radiation is by no means so dead as in my youth we thought it was. Some radiation is certainly corpuscular, and even the etherial kind shows indications, which may be misleading, that it is spotty, or locally concentrated into points, as if the wave front consisted of detached specks or patches; or, as J. J. Thomson says, "the wave-front must be more analogous to bright specks on a dark ground than to a uniformly illuminated surface," thus suggesting that the Ether may be fibrous in structure, and that a wave runs along lines of electric force; as the genius of Faraday surmised might be possible, in his "Thoughts on Ray Vibrations." Indeed, Newton guessed something of the same kind, I fancy, when he superposed ether-pulses on his corpuscles.

Whatever be the truth in this matter, a discussion on Radiation, of extreme weight and interest, though likewise of great profundity and technicality, is expected on Friday in Section A. We welcome Prof. Lorentz, Dr. Arrhenius, Prof. Langevin, Prof. Pringsheim, and others, some of whom have been specially invited to England because of the important contributions which they have made to the subject-matter of this discussion.

Why is so much importance attached to Radiation? Because it is the best-known and longest-studied link between matter and ether, and the only property we are acquainted with that affects the unmodified great mass of ether alone. Electricity and magnetism are associated with the modifications or singularities called electrons; most phenomena are connected still more directly with matter. Radiation, however, though excited by an accelerated electron, is subsequently let loose in the ether of space, and travels as a definite thing at a measurable and constant pace—a pace independent of everything so long as the ether is free, unmodified, and unloaded by matter. Hence radiation has much to teach us, and we have much to learn concerning its nature.

How far can the analogy of granular, corpuscular, countable, atomic, or discontinuous things be pressed? There are those who think it can be pressed very far. But to avoid misunderstanding let me state, for what it may be worth, that I myself am an upholder of *ultimate* Continuity, and a fervent believer in the Ether of Space.

We have already learnt something about the ether; and although there may be almost as many varieties of opinion as there are people qualified to form one, in my view we have learnt as follows:—

The Ether is the universal connecting medium which binds the universe together, and makes it a coherent whole instead of a chaotic collection of independent isolated fragments. It is the vehicle of transmission of all manner of force, from gravitation down to cohesion and chemical affinity; it is therefore the storehouse of potential energy.

Matter moves, but Ether is strained.

What we call elasticity of matter is only the result of an alteration of configuration due to movement and re-adjustment of particles, but all the strain and stress are in the ether. The ether itself does not move, that is to say, it does not move in the sense of locomotion, though it is probably in a violent state of rotational or turbulent motion in its smallest parts; and to that motion its exceeding rigidity is due.

As to its density, it must be far greater that that of any form of matter, millions of times denser than lead or platinum. Yet matter moves through it with perfect freedom, without any friction or viscosity. There is nothing paradoxical in this: viscosity is not a function o density; the two are not necessarily connected. When a solid moves through an alien fluid it is true that it acquires a spurious or apparent extra inertia from the fluid it displaces; but, in the case of matter and ether, not only is even the densest matter excessively porous and discontinuous, with vast interspaces in and among the atoms, but the constitution of matter is such that there appears to be no displacement in the ordinary sense at all; the ether is itself so modified as *to constitute* the matter in some way. Of course that portion moves, its inertia is what we observe, and its amount depends on the potential energy in its associated electric field, but the motion is not like that of a foreign body, it is that of some inherent and merely individualised portion of the stuff itself. Certain it is that the ether exhibits no trace of viscosity.*

Matter in motion, Ether under strain, constitute the fundamental concrete things we have to do with in physics. The first pair represent kinetic energy, the second potential energy; and all the activities of the material universe are represented by alternations from one of these forms to the other.

Whenever this transference and transformation of energy occur, work is done, and some effect is produced, but the energy is never diminished in quantity; it is merely passed on from one body to another, always from ether to matter or vice versa,—except in the case of radiation, which simulates matter—and from one form to another.

The forms of energy can be classified as either a translation, a rotation, or a vibration of pieces of matter of different sizes, from stars and planets down to atoms and electrons; or else an etherial strain which in various different ways is manifested by the behaviour of such masses of matter as appeal to our senses.†

Some of the facts responsible for the suggestion that energy is atomic seem to me to depend on the discontinuous nature of the structure of a material atom, and on the high velocity of its constituent particles. The apparently discontinuous emission of radiation is, I believe, due to features in the real discontinuity of matter. Disturbances inside an atom appear to be essentially catastrophic; a portion is liable to be ejected with violence. There appears to be a critical velocity below which ejection does not take place; and, when it does, there also occurs a sudden re-arrangement of parts which is presumably responsible for some perceptible etherial radiation. Hence it is, I suppose, that radiation comes off in gushes or bursts; and hence it appears to consist of indivisible units. The occasional phenomenon of new stars, as compared with the steady orbital motion of the millions of recognised bodies, may be suggested as an astronomical analogue.

The hypothesis of *quanta* was devised to reconcile the law that the energy of a group of colliding molecules must in the long run be equally shared among all their degrees of freedom, with the observed fact that the energy is really shared into only a small number of equal parts. For if vibration-possibilities have to be taken into account, the number of degrees of molecular freedom must be very large, and energy shared among them ought soon to be all frittered away; whereas it is not. Hence the idea is suggested that minor degrees of freedom are initially excluded from sharing the energy, because they cannot be supplied with less than one atom of it.

I should prefer to express the fact by saying that the ordinary encounters of molecules are not of a kind able to excite atomic vibrations, or in any way to disturb the ether. Spectroscopic or luminous vibrations of an atom are excited only by an exceptionally violent kind of collision, which may be spoken of as chemical clash; the ordinary molecular orbital encounters, always going on at the rate

* For details of my experiment on this subject see *Phil. Trans. Roy. Soc.* for 1893 and 1897; or a very abbreviated reference to it and to the other matters above-mentioned in my small book "The Ether of Space."

† See, in the *Philosophical Magazine* for 1879, my article on "A Classification of the Forms of Energy."

of millions a second, are ineffective in that respect, except in the case of phosphorescent or luminescent substances. That common molecular deflections *are* ineffective is certain, else all the energy would be dissipated or transferred from matter into the ether; and the reasonableness of their radiative inefficiency is not far to seek, when we consider the comparatively leisurely character of molecular movements, at speeds comparable with the velocity of sound. Admittedly, however, the effective rigidity of molecules must be complete, otherwise the sharing of energy must ultimately occur. They do not seem able to be set vibrating by anything less than a certain minimum stimulus; and that is the basis for the theory of *quanta*.

Quantitative applications of Planck's theory, to elucidate the otherwise shaky stability of the astronomically constituted atom, have been made; and the agreement between results so calculated and those observed, including a determination of series of spectrum lines, is very remarkable. One of the latest contributions to this subject is a paper by Dr. Bohr in the *Philosophical Magazine* for July this year.

To show that I am not exaggerating the modern tendency towards discontinuity, I quote from Poincaré's *Dernières Pensées*, a proposition which he announces in italics as representing a form of Prof. Planck's view of which he apparently approves:—

> "A physical system is susceptible of a finite number only of distinct conditions; it jumps from one of these conditions to another without passing through a continuous series of intermediate conditions."

Also this from Sir Joseph Larmor's Preface to Poincaré's *Science and Hypothesis*:—

> "Still more recently it has been found that the good Bishop Berkeley's logical gibes against the Newtonian ideas of fluxions and limiting ratios cannot be adequately appeased in the rigorous mathematical conscience, until our apparent continuities are resolved mentally into discrete aggregates which we only partially apprehend. The irresistible impulse to atomise everything thus proves to be not merely a disease of the physicist; a deeper origin, in the nature of knowledge itself, is suggested."

One very valid excuse for this prevalent attitude is the astonishing progress that has been made in actually seeing or almost seeing the molecules, and studying their arrangement and distribution.

The laws of gases have been found to apply to emulsions and to fine powders in suspension, of which the Brownian movement has long been known. This movement is caused by the orthodox molecular bombardment, and its average amplitude exactly represents the theoretical mean free path calculated from the "molecular weight" of the relatively gigantic particles. The behaviour of these microscopically visible masses corresponds closely and quantitatively with what could be predicted for them as fearfully heavy atoms, on the kinetic theory of gases; they may indeed be said to constitute a gas with a grm.-molecule as high as 200,000 tons; and, what is rather important as well as interesting, they tend visibly to verify the law of equipartition of energy even in so extreme a case, when that law is properly stated and applied.

Still more remarkable—the application of X-rays to display the arrangement of molecules in crystals, and ultimately the arrangement of atoms in molecules, as initiated by Prof. Laue with Drs. Friedrich and Knipping, and continued by Prof. Bragg and his son and by Dr. Tutton, constitute a series of researches of high interest and promise. By this means many of the theoretical anticipations of our countryman, Mr. William Barlow, and—working with him—Prof. Pope, as well as of those distinguished crystallographers von Groth and von Fedorow, have been confirmed in a striking way. These brilliant researches, which seem likely to constitute a branch of Physics in themselves, and which are being continued by Messrs. Moseley and C. G. Darwin, and by Mr. Keene and others, may be called an apotheosis of the atomic theory of matter.

One other controversial topic I shall touch upon in the domain of physics, though I shall touch upon it lightly, for it is not a matter for easy reference as yet. If the *Principle of Relativity* in an extreme sense establishes itself, it seems as if even Time would become discontinuous and be supplied in atoms, as money is doled out in pence or centimes instead of continuously;—in which case our customary existence will turn out to be no more really continuous than the events on a kinematograph screen,—while that great agent of continuity, the Ether of Space, will be relegated to the museum of historical curiosities.

In that case differential equations will cease to represent the facts of nature, they will have to be replaced by Finite Differences, and the most fundamental revolution since Newton will be inaugurated.

Now in all the debateable matters of which I have indicated possibilities I want to urge a conservative attitude. I accept the new experimental results on which some of these theories—such as the Principle of Relativity—are based, and am profoundly interested in them, but I do not feel that they are so revolutionary as their propounders think. I see a way to retain the old and yet embrace the new, and I urge moderation in the uprooting and removal of landmarks.

And of these the chief is Continuity. I cannot imagine the exertion of mechanical force across empty space, no matter how minute; a continuous medium seems to me essential. I cannot admit discontinuity in either Space or Time, nor can I imagine any sort of experiment which would justify such a hypothesis. For surely we must realise that we know nothing experimental of either space or time, we cannot modify them in any way. We make experiments on bodies, and only on bodies, using "body" as an exceedingly general term.

We have no reason to postulate anything but continuity for space and time. We cut them up into conventional units for convenience sake, and those units we can count; but there is really nothing atomic or countable about the things themselves. We can count the rotations of the earth, or the revolutions of an electron, or the vibrations of a pendulum, or the waves of light. All these are concrete and tractable physical entities; but space and time are ultimate data, abstractions based on experience. We know them through motion, and through motion only, and motion is essentially continuous. We ought clearly to discriminate between things themselves and our mode of measuring them. Our measures and perceptions may be affected by all manner of incidental and trivial causes, and we may get confused or hampered by our own movement; but there need be no such complication in things themselves, any more than a landscape is distorted by looking at it through an irregular window-pane or from a travelling coach. It is an ancient and discarded fable that complications introduced by the motion of an observer are real complications belonging to the outer universe.

Very well, then, what about the Ether, is that in the same predicament? Is that an abstraction, or a mere convention, or is it a concrete physical entity on which we can experiment?

Now it has to be freely admitted that it is exceedingly difficult to make experiments on the ether. It does not appeal to sense, and we know no means of getting hold of it. The one thing we know metrical about it is the velocity with which it can transmit transverse waves. That is clear and definite, and thereby to my judgment it proves itself a physical agent; not indeed tangible or sensible, but yet concretely real.

But it does elude our laboratory grasp. If we rapidly move matter through it, hoping to grip it and move it too, we fail; there is no mechanical connexion. And even if we experiment on light we fail too. So long as transparent matter is moving relatively to us, light can be affected inside that matter; but when matter is relatively stationary

to matter nothing observable takes place, however fast things may be moving, so long as they move together.

Hence arises the idea that motion with respect to Ether is meaningless: and the fact that only relative motion of pieces of matter with respect to each other has so far been observed is the foundation of the Principle of Relativity. It sounds simple enough as thus stated, but in its developments it is an ingenious and complicated doctrine embodying surprising consequences which have been worked out by Professor Einstein and his disciples with consummate ingenuity.

What have I to urge against it? Well, in the first place, it is only in accordance with common sense that no effect of the first order can be observed without relative motion of matter. An Ether-stream through our laboratories is optically and electrically undetectable, at least as regards first order observation; this is clearly explained for general readers in my book *The Ether of Space*, Chapter IV. But the Principle of Relativity says more than that, it says that no effect of any order of magnitude can ever be observed without the relative motion of matter.

The truth underlying this doctrine is that absolute motion without reference to *anything* is unmeaning. But the narrowing down of "anything" to mean any piece of matter is illegitimate. The nearest approach to absolute motion that we can physically imagine is motion through or with respect to the Ether of Space. It is natural to assume that the Ether is on the whole stationary, and to use it as a standard of rest; in that sense motion with reference to it may be called absolute, but in no other sense.

The Principle of Relativity claims that we can never ascertain such motion: in other words, it practically or pragmatically denies the existence of the Ether. Every one of our scientifically observed motions, it says, are of the same nature as our popularly observed ones, *viz.*, motion of pieces of matter relatively to each other; and that is all that we can ever know. Everything goes on—says the Principle of Relativity—as if the Ether did not exist.

Now the facts are that no motion with reference to the ether alone has ever yet been observed: there are always curious compensating effects which just cancel out the movement-terms and destroy or effectively mask any phenomenon that might otherwise be expected. When matter moves past matter observation can be made; but, even so, no consequent locomotion of ether, outside the actually moving particles, can be detected.

(It is sometimes urged that rotation is a kind of absolute motion that can be detected, even in isolation. It can so be detected, as Newton pointed out; but in cases of rotation matter on one side the axis is moving in the opposite direction to matter on the other side of the axis; hence rotation involves relative material motion, and therefore can be observed).

To detect motion through ether we must use an etherial process. We may use radiation, and try to compare the speeds of light along or across the motion; or we might try to measure the speed, first with the motion and then against it. But how are we to make the comparison? If the time of emission from a distant source is given by a distant clock, that clock must be observed through a telescope, that is by a beam of light; which is plainly a compensating process. Or the light from a neighbouring source can be sent back to us by a distant mirror; when again there will be compensation. Or the starting of light from a distant terrestrial source may be telegraphed to us, either with a wire or without; but it is the ether that conveys the message in either case, so again there will be compensation. Electricity, Magnetism, and Light, are all effects of the ether.

Use Cohesion, then; have a rod stretching from one place to another, and measure that. But cohesion is transmitted by the ether too, if, as believed, it is the universal binding medium. Compensation is likely; compensation can, on the electrical theory of matter, be predicted.

Use some action not dependent on Ether, then. Very well, where shall we find it?

To illustrate the difficulty I will quote a sentence from Sir Joseph Larmor's paper before the International Congress of Mathematicians at Cambridge last year.

> "If it is correct to say with Maxwell that all radiation is an electrodynamic phenomenon, it is equally correct to say with him that all electrodynamic relations between material bodies are established by the operation on the molecules of those bodies, of fields of force which are propagated in free space as radiation, and in accordance with the laws of radiation, from one body to the other."

The fact is we are living in an epoch of some very comprehensive generalisations. The physical discovery of the twentieth century, so far, is the Electrical Theory of Matter. This is the great new theory of our time; it was referred to, in its philosophical aspect, by Mr. Balfour in his Presidential Address at Cambridge in 1904. We are too near it to be able to contemplate it properly; it has still to establish itself and to develop in detail, but I anticipate that in some form or other it will prove true.*

Here is a briefest possible summary of the first chapter (so to speak) of the Electrical Theory of Matter.

1. Atoms of Matter are composed of electrons,—of positive and negative electric charges.
2. Atoms are bound together into molecules by chemical affinity which is intense electrical attraction at ultra-minute distances.
3. Molecules are held together by cohesion, which I for one regard as residual or differential chemical affinity over molecular distances.
4. Magnetism is due to the locomotion of electrons. There is no magnetism without an electric current, atomic or otherwise. There is no electric current without a moving electron.
5. Radiation is generated by every accelerated electron, in amount proportional to the square of its acceleration; and there is no other kind of radiation, except indeed a corpuscular kind; but this depends on the velocity of electrons, and therefore again can only be generated by their acceleration.

The theory is bound to have curious consequences; and already it has contributed to some of the uprooting and uncertainty that I speak of. For, if it be true, every material interaction will be electrical, *i.e.*, etherial; and hence arises our difficulty. Every kind of force is transmitted by the ether, and hence, so long as all our apparatus is travelling together at one and the same pace, we have no chance of detecting the motion. That is the strength of the Principle of Relativity. The changes are not zero, but they cancel each other out of observation.

Many forms of statement of the famous Michelson-Morley experiment are misleading. It is said to prove that the time taken by light to go with the ether stream is the same as that taken to go against or across it. It does not show that. What it shows is that the time taken by light to travel to and fro on a measured interval fixed on a rigid block of matter is independent of the aspect of that block with respect to any motion of the earth through space. A definite and most interesting result; but it may be, and often is, interpreted loosely and too widely.

It is interpreted too widely, as I think, when Professor Einstein goes on to assume that no non-relative motion of matter can be ever observed even when *light* is brought into consideration. The relation of light to matter is very curious. The wave front of a progressive wave simulates many of the properties of matter. It has energy, it has momentum, it exerts force, it sustains reaction. It has been described as a portion of the mass of a radiating body,—which gives it a curiously and unexpectedly corpuscular "feel." But it has a definite velocity. Its velocity in space relative to the ether is an absolute constant independent of the motion of the source. This would not be true for corpuscular light.

* For a general introductory account of the electrical theory of matter my Romanes Lecture for 1913 (Clarendon Press) may be referred to.

Hence I hold that here is something with which our own motion may theoretically be compared; and I predict that our motion through the ether will some day be detected by help of this very fact,—by comparing our speed with that of light: though the old astronomical aberration, which seemed to make the comparison easy, failed to do so quite simply, because it is complicated by the necessity of observing the position of a distant source, in relation to which the earth is moving. If the source and observer are moving together there is no possibility of observing aberration. Nevertheless, I maintain that when matter is moving near a beam of light we may be able to detect the motion. For the velocity of light in space is no function of the velocity of the source, nor of matter near it; it is quite unaffected by source or receiver. Once launched it travels in its own way. If we are travelling to meet it, it will be arriving at us more quickly; if we travel away from it, it will reach us with some lag. And observation of the acceleration or retardation is made by aid of Jupiter's satellites. We have there the dial of a clock, to or from which we advance or recede periodically. It gains while we approach it, it loses while we recede from it, it keeps right time when we are stationary or only moving across the line of sight.

But then of course it does not matter whether Jupiter is standing still and we are moving, or vice versa; it is a case of relative motion of matter again. So it is if we observe a Doppler effect from the right and left hand limbs of the rotating sun. True, and if we are to permit no relative motion of matter we must use a terrestrial source, clamped to the earth as our receiver is. And now we shall observe nothing.

But not because there is nothing to observe. Lag must really occur if we are running away from the light, even though the source is running after us at the same pace; unless we make the assumption,—true only for corpuscular light,—that the velocity of light is not an absolute thing, but is dependent on the speed of the source. With corpuscular light there is nothing to observe; with wave light there is something, but we cannot observe it.

But if the whole solar system is moving through the ether I see no reason why the relative ether drift should not be observed by a differential residual effect in connection with Jupiter's satellites or the right and left limbs of the sun. The effect must be too small to observe without extreme precision, but theoretically it ought to be there. Inasmuch, however, as relative motion of matter with respect to the observer is involved in these effects it may be held that the detection of a uniform drift of the solar system in this way is not contrary to the Principle of Relativity. It is contrary to some statements of that Principle; and the cogency of those statements breaks down, I think, whenever they include the velocity of light; because there we really have something absolute (in the only sense in which the term can have a physical meaning) with which we can compare our own motions, when we have learnt how.

But in ordinary astronomical translation—translation as of the earth in its orbit—all our instruments, all our standards, the whole contents of our laboratory, are moving at the same rate in the same direction; under those conditions we cannot expect to observe anything. Clerk Maxwell went so far as to say that if every particle of matter simultaneously received a graduated blow so as to produce a given constant acceleration all in the same direction, we should be unaware of the fact. He did not then know all that we know about radiation. But apart from that, and limiting ourselves to comparatively slow changes of velocity, our standards will inevitably share whatever change occurs. So far as observation goes, everything will be practically as if no change had occurred at all; though that may not be the truth. All that experiment establishes is that there have so far always been compensations; so that the attempt to observe motion through the ether is being given up as hopeless.

Surely, however, the minute and curious compensations cannot be accidental, they must be necessary? Yes, they are necessary; and I want to say why. Suppose the case were one of measuring thermal expansion; and suppose everything had the same temperature and the same expansibility; our standards would contract or expand with everything else, and we could observe nothing; but expansion would occur nevertheless. That is obvious, but the following assertion is not so obvious. If everything in the Universe had the same temperature, no matter what that temperature was, nothing would be visible at all; the external world, so far as vision went, would not appear to exist. Visibility depends on radiation, on differential radiation. We must have differences to appeal to our senses, they are not constructed for uniformity.

It is the extreme omnipresence and uniformity and universal agency of the ether of space that makes it so difficult to observe. To observe anything you must have differences. If all actions at a distance are conducted at the same rate through the ether, the travel of none of them can be observed. Find something not conveyed by the ether and there is a chance. But then every physical action is transmitted by the ether, and in every case by means of its transverse or radiation-like activity.

Except perhaps Gravitation. That may give us a clue some day, but at present we have not been able to detect its speed of transmission at all. No plan has been devised for measuring it. Nothing short of the creation or destruction of matter seems likely to serve; creation or destruction of the gravitational unit, whether it be an atom or an electron or whatever it is. Most likely the unit of weight is an electron, just as the unit of mass is.

The so-called non-Newtonian Mechanics, with mass and shape a function of velocity, is an immediate consequence of the electrical theory of matter. The dependence of inertia and shape on speed is a genuine discovery, and, I believe, a physical fact. The Principle of Relativity would reduce it to a conventional fiction. It would seek to replace this real change in matter by imaginary changes in time. But surely we must admit that Space and Time are essentially unchangeable; they are not at the disposal even of mathematicians; though it is true that Pope Gregory, or a Daylight-saving Bill, can play with our units, can turn the 3rd of October in any one year into the 14th, or can make the sun South sometimes at eleven o'clock sometimes at twelve.*

But the changes of dimension and mass due to velocity are not conventions, but realities; so I urge, on the basis of the electrical theory of matter. The Fitzgerald-Lorentz hypothesis I have an affection for. I was present at its birth. Indeed I assisted at its birth; for it was in my study at 21, Waverley Road, Liverpool, with Fitzgerald in an arm chair, and while I was enlarging on the difficulty of reconciling the then new Michelson experiment with the theory of astronomical aberration and with other known facts, that he made his brilliant surmise:—"Perhaps the stone slab was affected by the motion." I rejoined that it was a 45° shear that was needed. To which he replied, "Well, that's all right—a simple distortion." And very soon he said, "And I believe it occurs, and that the Michelson experiment demonstrates it." A shortening long-ways, or a lengthening cross-ways would do what was wanted.

And is such a hypothesis gratuitous? Not at all; in the light of the electrical theory of matter such an effect ought to occur. The amount required by the experiment, and given by the theory, is equivalent to a shrinkage of the earth's diameter by rather less than 3 inches, in the line of its orbital motion through the ether of space. An oblate spheroid with the proper excentricity has all the simple geometrical properties of a stationary sphere; the

* In the historical case of governmental interference with the calendar, no wonder the Populace rebelled. Surely someone might have explained to the authorities that dropping leap year for the greater part of a century would do all that was wanted, and that the horrible inconvenience of upsetting all engagements and shortening a single year by eleven days could be avoided.

excentricity depends in a definite way on speed, and becomes considerable as the velocity of light is approached.

All this Profs. Lorentz and Larmor very soon after, and quite independently, perceived; though this is only one of the minor achievements in the electrical theory of matter which we owe to our distinguished visitor Prof. H. A. Lorentz.

The key of the position, to my mind, is the nature of cohesion. I regard cohesion as residual chemical affinity, a balance of electrical attraction over repulsion between groups of alternately charged molecules. Lateral electrical attraction is diminished by motion; so is lateral electric repulsion. In cohesion both are active, and they nearly balance. At anything but molecular distance they quite balance, but at molecular distance attraction predominates. It is the diminution of the predominant partner that will be felt. Hence, while longitudinal cohesion, or cohesion in the direction of motion, remains unchanged, lateral cohesion is less; so there will be distortion, and a unit cube $x\ y\ z$ moving along x with velocity u becomes a parallelopiped with sides $1/k^2$, k, k; where $1/k^2 = 1 - u^2/v^2$.*

The electrical theory of matter is a positive achievement, and has positive results. By its aid we make experiments which throw light upon the relation between matter and the Ether of Space. The Principle of Relativity, which seeks to replace it, is a principle of negation, a negative proposition, a statement that observation of certain facts can never be made, a denial of any relation between matter and ether, a virtual denial that the ether exists. Whereas if we admit the real changes that go on by reason of rapid motion, a whole field is open for discovery; it is even possible to investigate the changes in shape of an electron—appallingly minute though it is—as it approaches the speed of light; and properties belonging to the Ether of Space, evasive though it be, cannot lag far behind.

Speaking as a physicist I must claim the Ether as peculiarly our own domain. The study of molecules we share with the chemist, and matter in its various forms is investigated by all men of science, but a study of the ether of space belongs to physics only. I am not alone in feeling the fascination of this portentous entity. Its curiously elusive and intangible character, combined with its universal and unifying permeance, its apparently infinite extent, its definite and perfect properties, make the ether the most interesting as it is by far the largest and most fundamental ingredient in the material cosmos.

As Sir J. J. Thomson said at Winnipeg—

> "The ether is not a fantastic creation of the speculative philosopher; it is as essential to us as the air we breathe. . . . The study of this all-pervading substance is perhaps the most fascinating and important duty of the physicist."

Matter it is not, but material it is; it belongs to the material universe and is to be investigated by ordinary methods. But to say this is by no means to deny that it may have mental and spiritual functions to subserve in some other order of existence, as Matter has in this.

The ether of space is at least the great engine of continuity. It may be much more, for without it there could hardly be a material universe at all. Certainly, however, it is essential to continuity; it is the one all-permeating substance that binds the whole of the particles of matter together. It is the uniting and binding medium without which, if matter could exist at all, it could exist only as chaotic and isolated fragments; and it is the universal medium of communication between worlds and particles. And yet it is possible for people to deny its existence, because it is unrelated to any of our senses, except sight, and to that only in an indirect and not easily recognised fashion.

To illustrate the thorough way in which we may be unable to detect what is around us unless it has some link or bond which enables it to make appeal, let me make another quotation from Sir J. J. Thomson's Address at Winnipeg in 1909. He is leading up to the fact that even single atoms, provided they are fully electrified with the proper atomic charge, can be detected by certain delicate instruments—their field of force bringing them within our ken—whereas a whole crowd of unelectrified ones would escape observation.

> "The smallest quantity of unelectrified matter ever detected is probably that of neon, one of the inert gases of the atmosphere. Prof. Strutt has shown that the amount of neon in 1/20 of a cubic centimetre of the air at ordinary pressures can be detected by the spectroscope. Sir William Ramsay estimates that the neon in the air only amounts to one part of neon in 100,000 parts of air, so that the neon in 1/20 of a cubic centimetre of air would only occupy at atmospheric pressure a volume of half a millionth of a cubic centimetre. When stated in this form the quantity seems exceedingly small, but in this small volume there are about ten million million molecules. Now the population of the earth is estimated at about fifteen hundred millions, so that the smallest number of molecules of neon we can identify is about 7000 times the population of the earth. In other words, if we had no better test for the existence of a man than we have for that of an unelectrified molecule we should come to the conclusion that the earth is uninhabited."

The parable is a striking one, for on these lines it might legitimately be contended that we have no right to say positively that even space is uninhabited. All we can safely say is that we have no means of detecting the existence of non-planetary immaterial dwellers, and that unless they have some link or bond with the material they must always be physically beyond our ken. We may therefore for practical purposes legitimately treat them as non-existent until such link is discovered, but we should not dogmatise about them. True agnosticism is legitimate, but not the dogmatic and positive and gnostic variety.

For I hold that Science is incompetent to make comprehensive denials, even about the Ether, and that it goes wrong when it makes the attempt. Science should not deal in negations; it is strong in affirmations, but nothing based on abstraction ought to presume to deny outside its own region. It often happens that things abstracted from and ignored by one branch of science may be taken into consideration by another:—

Thus, Chemists ignore the Ether.
Mathematicians may ignore experimental difficulties.
Physicists ignore and exclude live things.
Biologists exclude Mind and Design.
Psychologists may ignore human origin and human destiny.
Folk-lore students and comparative Mythologists need not trouble about what modicum of truth there may be in the legends which they are collecting and systematising.
And Microscopists may ignore the stars.

Yet none of these ignored things should be denied.

Denial is no more infallible than assertion. There are cheap and easy kinds of scepticism, just as there are cheap and easy kinds of dogmatism; in fact scepticism can become viciously dogmatic, and science has to be as much on its guard against personal predilection in the negative as in the positive direction. An attitude of universal denial may be very superficial.

> "To doubt everything or to believe everything are two equally convenient solutions; both dispense with the necessity of reflection."

* Different modes of estimating the change give slightly different results; some involve a compression as well as a distortion—in fact, the strain associated with the name of Thomas Young; the details are rather complicated and this is not the place to discuss them. A pure shear, of magnitude specified in the text, is simplest, it is in accord with all the experimental facts—including some careful measurements by Bucherer—and I rather expect it to survive.

All intellectual processes are based on abstraction. For instance, History must ignore a great multitude of facts in order to treat any intelligently: it selects. So does Art; and that is why a drawing is clearer than reality. Science makes a diagram of reality, displaying the works like a skeleton clock. Anatomists dissect out the nervous system, the blood vessels, and the muscles, and depict them separately,—there must be discrimination for intellectual grasp,—but in life they are all merged and co-operating together; they do not really work separately, though they may be studied separately. A scalpel discriminates: a dagger or a bullet crashes through everything. That is life,—or rather death. The laws of nature are a diagrammatic framework, analysed or abstracted out of the full comprehensiveness of reality.

Hence it is that Science has no authority in denials. To deny effectively needs much more comprehensive knowledge than to assert. And abstraction is essentially not comprehensive; one cannot have it both ways. Science employs the methods of abstraction and thereby makes its discoveries.

The reason why some physiologists insist so strenuously on the validity and self-sufficiency of the laws of physics and chemistry, and resist the temptation to appeal to unknown causes—even though the guiding influence and spontaneity of living things are occasionally conspicuous as well as inexplicable—is that they are keen to do their proper work; and their proper work is to pursue the laws of ordinary physical Energy into the intricacies of "colloidal electrolytic structures of great chemical complexity," and to study its behaviour there.

What we have clearly to grasp, on their testimony, is that for all the terrestrial manifestations of life the ordinary physical and chemical processes have to serve. There are not new laws for living matter, and old laws for non-living, the laws are the same; or if ever they differ, the burden of proof rests on him who sustains the difference. The conservation of energy, the laws of chemical combination, the laws of electric currents, of radiation, etc., etc.,—all the laws of Chemistry and Physics—may be applied without hesitation in the Organic domain. Whether they are sufficient is open to question, but as far as they go they are necessary; and it is the business of the physiologist to seek out and demonstrate the action of those laws in every vital action.

This is clearly recognised by the leaders, and in the definition of Physiology by Burdon Sanderson he definitely limited it to the study of "ascertainable characters of a chemical and physical type." In his Address to the Sub-section of Anatomy and Physiology at York in 1881 he spoke as follows:—

> "It would give you a true idea of the nature of the great advance which took place about the middle of this century if I were to define it as the epoch of the death of 'vitalism.' Before that time, even the greatest biologists—*e.g.*, J. Müller—recognised that the knowledge biologists possessed both of vital and physical phenomena was insufficient to refer both to a common measure. The method therefore was to study the processes of life in relation to each other only. Since that time it has become fundamental in our science not to regard any vital process as understood at all unless it can be brought into relation with physical standards, and the methods of physiology have been based exclusively on this principle. The most efficient cause [conducing to the change] was the progress which had been made in physics and chemistry, and particularly those investigations which led to the establishment of the doctrine of the Conservation of Energy." . . . .
>
> "Investigators who are now working with such earnestness in all parts of the world for the advance of physiology, have before them a definite and well-understood purpose, that purpose being to acquire an exact knowledge of the chemical and physical processes of animal life and of the self-acting machinery by which they are regulated for the general good of the organism. The more singly and straightforwardly we direct our efforts to these ends, the sooner we shall attain to the still higher purpose—the effectual application of our knowledge for the increase of human happiness."

Professor Gotch, whose recent loss we have to deplore, puts it more strongly:—

> "It is essentially unscientific," he says, "to say that any physiological phenomenon is caused by vital force."

(To be continued).

A GENERAL METHOD FOR THE PREPARATION OF THE AMMONIUM SALTS OF ORGANIC ACIDS.

By EDWARD H. KEISER and L. McMASTER.

The usual method of preparing the ammonium salts of organic acids, namely, neutralising the aqueous solution of the acid with ammonia and evaporating to crystallisation, gives very unsatisfactory results owing to the hydrolytic action of water upon these salts. A study of the literature of ammonium salts of organic acids shows that comparatively few of them have been made and analysed. In the case of dibasic acids usually only the acid ammonium salt has been prepared.

In attempting to prepare the amide of maleic acid we desired to start with the diammonium maleate, but found it impossible to make this salt by neutralising a solution of maleic acid with ammonia and evaporating to crystallisation. We therefore dissolved the acid in ether and conducted a stream of dry ammonia gas into the ethereal solution. A white flocculent rather gelatinous precipitate at first formed, this soon collected into lumps, and, on continuing to pass in ammonia, changed into a white crystalline powder. Analysis showed it to be diammonium maleate.

This method of preparing diammonium maleate was found to be applicable in a general way to the preparation of the ammonium salts of other organic acids. In those cases in which the acid was insoluble in ether some other solvent, such as absolute alcohol, or a mixture of ether and alcohol, was used. The method is dependent upon the fact that most organic acids are soluble in ether or alcohol or a mixture of the two, while the ammonium salts are insoluble and can be thrown down by means of a stream of dry ammonia gas. Very good yields are obtained by this method. The organic salts of other weak bases, such as the salts of aniline, the amines, and other organic bases can, no doubt, be made in the same general way by doing away with aqueous solutions and using only alcoholic or ethereal solutions of both acid and base.

We have made, in this way, the ammonium salts of maleic, fumaric, mesaconic, citraconic, malonic, and phthalic acids.

Ammonium Maleate.—This salt was precipitated from the ethereal solution of the acid by a stream of dry ammonia, as described above, washed on the filter with ether, and dried in the air. It is a white crystalline powder, not deliquescent in the air but readily soluble in water. Büchner (*Liebig's Ann. Chem.*, xlix., 67) describes this salt as being deliquescent, but his compound was prepared in the wet way. This salt has an odour similar to that of acetamide.

Analyses gave the following results:—

	C.	H.	N.
Calculated for $C_2H_2(CO_2NH_4)_2$	31·97	6·71	18·66
Found—I.	—	—	16·12
II.	31·20	7·09	16·13
III.	32·04	6·89	18·70
IV.	32·06	6·91	18·46

The first two nitrogen determinations were made by the Kjeldahl method and gave low results, the last two by the Dumas method. We also prepared this salt by precipitation with ammonia in a solution of the acid in absolute alcohol.

Ammonium Fumarate.—Fumaric acid was dissolved in absolute alcohol and dry ammonia conducted into the solution. A heavy white amorphous powder was at once formed. It was filtered, washed thoroughly with alcohol and ether, and dried in air on a porous plate. This salt has no odour, as in the case of the diammonium maleate. It is not deliquescent, but dissolves readily in water. It gave on analysis the following results:—

N calculated for $C_2H_2(CO_2NH_4)_2$	18·66
Found—I.	18·47
II.	18·50

Ammonium Mesaconate.—The mesaconic acid, obtained from Kahlbaum, was dissolved in ether and dry ammonia conducted into the solution. A gelatinous precipitate was at first formed, but this soon changed into a crystalline powder. The salt was filtered, washed on the filter with ether, and then dried in the air. Like the ammonium fumarate it had no odour. It was not deliquescent, but dissolved readily in water. Determinations of nitrogen gave the following results:—

N calculated for $CH_3C_2H(CO_2NH_4)_2$ ..	17·07
Found—I.	16·71
II.	16·84

Ammonium Citraconate.—Citraconic acid (Kahlbaum) was dissolved in ether and ammonia passed into the solution. A thick colloidal solution was at first formed, but as the ammonia continued to pass into the solution this changed into a crystalline precipitate. This was filtered, washed with ether, and dried in the air. Like the ammonium maleate it has an odour like that of acetamide. The salt is not deliquescent, but soluble in water.

N calculated for $CH_3C_2H(CO_2NH_4)_2$ ..	17·07
Found—I.	16·82
II.	16·87

The ammonium salts of malonic and phthalic acids were also made by the same general method. The ammonium malonate came down in ether solution as a fine white crystalline precipitate. It had no odour and was not deliquescent, although readily soluble in water. The ammonium phthalate was obtained as a white powder.—*American Chemical Journal*, xlix., No. 2.

NOTICES OF BOOKS.

Outline of Stationery Testing. By Henry Aldous Bromley. London: Charles Griffin and Co., Ltd. 1913.

This book gives a concise account of practical methods of testing stationery, and the author's experience as assistant examiner of paper to His Majesty's Stationery Office enables him to write authoritatively, and gives great weight to his hints and recommendations. No matter of purely theoretical interest is included in the book, which is intended specially for practical men, and only simple apparatus and methods are described, which, however, may be relied upon to give accurate results. The testing of paper by physical means is first discussed, and the Schopper and other machines which are used for determining the strength of paper are described and illustrated. In the chapter on microscopical methods plates showing the different fibres are given, with brief directions for the preparation and staining of specimens for examination. The chemical investigation of paper is treated in outline, and some notes are given on the characteristics and requirements of special papers. Other products, the testing of which is described, include inks, sealing-wax, string, and gums.

Report of the Woburn Experimental Station. I. Field Experiments, 1912. II. *Pot-culture Experiments*, 1910, 1911, 1912. By J. Augustus Voelcker, M.A., B.Sc., Ph.D. London: John Murray. 1913.

In this report the conclusions to be drawn from the field experiments conducted by the Woburn Experimental Station of the Royal Agricultural Society of England during 1912, the thirty-sixth consecutive season, are concisely stated. The experiments dealt with the continuous growing of wheat and barley, different varieties of cereals, the inoculation of leguminous crops, &c. The yield and quality of grain were in all cases below the average, although the root crops were unusually satisfactory. The more interesting part of the report is that which describes the Hills experiments upon the influence of the comparatively rare constituents of the soil upon wheat. As the result of several years' work it has been found that the salts of lithium exercise a stimulating effect, when the quantity present does not exceed 0·002 per cent. Above 0·003 per cent they are toxic in their action, the toxicity differing with different salts. Similar experiments with zinc salts give the same results, although their influence is very much less than that of lithium, and the general conclusion to be drawn from the whole series of experiments is that the influence of the rarer constituents of the soil upon vegetation is much greater than has hitherto been supposed.

The London Matriculation Directory, June, 1913. London: University Tutorial Press, Ltd.

This is the Sixty-fourth Number of the "London Matriculation Directory," and exhibits the same excellent features as those which have distinguished the earlier numbers. These include articles on the text-books in each subject, and hints to intending candidates as to the choice of subjects; the papers set in June, 1913, are reproduced in full, with solutions and criticisms of them, and in addition full information is given relating to the University Correspondence and Tutorial Colleges.

Science Conspectus. Vol. III., No. 3. Published by the Society of Arts of the Massachusetts Institute of Technology, Boston, Mass.

The aim of this periodical is to give a general survey of scientific work for educated readers who wish to keep abreast of recent advances in all branches. Most of the papers in this number are original, and are contributed by experts. They treat of such subjects as the importance of negative eugenics, the clam industry in Massachusetts, the Pyramids as an astronomical monument. Chemical science is represented by an interesting article on catalysis, in which the essential features of the phenomenon are described, and some possible explanations of its occurrence are put before the reader.

Notes on the Therapeutics of Radium in the Bath Waters. Compiled by John Hatton.

This handbook, published by the Corporation of Bath, has been compiled in order to place before the medical profession and the general public the results of recent investigations of the Hot Springs of Bath. It contains the report of Sir William Ramsay, in which the results of the analysis of the waters are stated, and suggestions are given of fresh methods of using the highly radio-active gas dissolved in the water. Other papers in the book are by Prof. Weiss on "The Balneological Aspect of Radium," and on "Radium Emanation and Physiological Processes," by Dr. S. Saubermann, and a brief list is given of the cases for which the waters of Bath are indicated.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Academie des Sciences. Vol. clvi., No. 25, June 23, 1913.

Phenomenon of Photocatalysis.—Max Landau.—Millinormal oxalic acid when exposed to the ultra-violet rays is decomposed 300 times more slowly than when exposed in presence of uranyl nitrate in equimolecular concentration. All compounds of uranium possess photocatalytic powers, and there is no parallelism between the photocatalytic power and the radio-active power of these compounds. Photocatalysis takes place even when the catalysts are insoluble, and the action is due exclusively to the cation. Some other metals were tested for the same power, but it was found that none of them was as strong as uranium.

Melting-points, Specific Heats, and Heats of Fusion of the Alkali Metals.—E. Rengade.—Very carefully performed determinations show that the atomic specific heats of the alkali metals increase slightly and regularly with the atomic weights, while the atomic heats of fusion decrease regularly. The ratio of the atomic heat of fusion to the absolute temperature of fusion is absolutely constant.

Oxidation of Alcohols under the Influence of Heat Alone.—J. B. Senderens.—When the temperature is raised the alcohols begin to undergo oxidation, the process beginning at 380° for amyl alcohol, 400° for isobutyl alcohol, and 405° for ethyl alcohol. All the oxygen of the air is absorbed by these alcohols at 410°, 435°, and 450° respectively. The chief product is CO, and a small amount of CO_2 is formed also. Certain substances such as magnesium, zinc, and aluminium, which have been supposed to be good catalysts, in reality act catalytically to only a very slight extent.

New Series of Isopyrazolones.—G. Favrel.—When dilute solutions of soda act on the hydrazones of the γ-chlorinated acetyl acetic ethers the latter are converted into isopyrazolones of a new type, which may be called 4-isopyrazolones. The γ-brominated acetyl acetic ethers give the same results, but with more difficulty.

Berichte der Deutschen Chemischen Gesellschaft. Vol. xlvi., No. 9, 1913.

New Hydrogen Boride, B_2H_6.—Alfred Stock and Kurt Friederici.—If gaseous hydrogen boride, B_4H_{10}, is kept for some time at room temperature over mercury the volume increases, and solid and gaseous products are obtained. The latter consist of hydrogen and a new boride, boiling at −87°, and having the formula B_2H_6. A convenient way to prepare the latter is to heat B_4H_{10} to 100° for some hours. It is a colourless gas of characteristic odour which recalls that of B_4H_{10}, and also of sulphuretted hydrogen. Its melting-point lies below −140°. It is much more stable than B_4H_{10}. When heated over an open flame it decomposes, giving colourless and yellow solid borides. It is decomposed by ultra-violet light and rapidly attacked by water, the following reaction occurring:—$B_2H_6 + 6H_2O = 2H_3BO_3 + 6H_2$. It does not ignite in air unless other hydrogen borides are present.

Sensitiveness to Light of the Nitrides of Silver, Mercurous Oxide, Lead, Cuprous Oxide, and of Basic Lead and Cupric Nitrides.—Lothar Wöhler and W. Krupko.—Silver nitride is very sensitive to light, and nitrogen is evolved when coloured products are produced in sun or mercury light. The sensitiveness of the product to a blow or to rise of temperature shows that it is not a new subnitride, but a mixture of unchanged normal nitride with finely divided metal of a colloidal nature. The meta can be detected microphotographically, especially the mercury drops from mercurous nitride. Cuprous nitride, which the authors have prepared for the first time, shows the same sensitiveness to light. Considerable quantities of ammonia are formed when lead nitride is exposed to light under water, owing to hydrolysis and the reduction of the acid by metallic lead. By heating lead or copper nitride with the hydroxide under water, basic nitrides, $PbOPbN_6$ and $CuOCuN_6$ are formed.

MISCELLANEOUS.

Schools of Chemistry.—The following additional information has been received:—

MANCHESTER SCHOOL OF TECHNOLOGY.—The School is established as the Faculty of Technology in the University of Manchester, and students of the School fulfilling the conditions can proceed to the Degrees of Bachelor and Master of Technical Science (B.Sc. Tech. and M.Sc. Tech.). Special facilities are offered to graduate students desirous of pursuing advanced research in any department of Applied Chemistry and other branches of the Industrial Arts, and a Journal is published embodying the more important results of such researches. The possession of a University Degree is of increasing importance to young men who are seeking the more important positions connected with the Chemical Industries. The supply of students entering the Chemical Department, although it has been steadily increasing for some years, has not kept pace with the demand for those who have completed the degree course. Thus the number of applications for young men who have graduated in Chemistry from the School of Technology was last year much in excess of the number of students graduating in this department. A similar excess of the demand over the supply is now being experienced in the Electrical Engineering Department, while the demand on the part of Mechanical Engineering firms for graduates in Mechanical Engineering is also making itself felt.

LEEDS: CENTRAL TECHNICAL SCHOOL, Leeds Institute, Cookridge Street, Leeds.—Head Master, R. E. Barnett, B.Sc. (Lond.), A.R.C.S. Evening Classes are held in all subjects of Science and Technology, among which are:—Chemistry (Inorganic and Organic), Chemical Calculations and Principles of Analysis, by W. W. Burrell, M.Sc., J. B. Murray, A. McFarlane, and G. H. Rydall, B.Sc.; Metallurgy (Theoretical and Practical) and Iron and Steel Manufacture, by B. A. Burrell, F.I.C., F.C.S., and T. O. Thornton; Gas Manufacture, by W. E. Pettigrew; Oils and Fats; Magnetism and Electricity, Practical Physics, &c., by J. E. Tindall, B.A., B.Sc.; Bread-making and Flour Confectionery, by W H. Quinn and J. C Hesselgrave; Photography and Process Work, by S. E. Bottomley and others. Fees: from 7s. 6d. per session. Group courses arranged for Students engaged in Chemical Industries. Special three-evening Course for Pharmaceutical Students, covering the "Minor" syllabus in three years, by J. H. Gough, Ph.C., F.C.S.; S. Parrish, B.Sc., A.R.C.S; and N. Walker. Session commences Sept. 22nd. See the Technical Handbook, 2d. (by post 5d.). Prospectuses of various Classes free on application to the Head Master, or to James Graham, Secretary for Education, Calverley Street, Leeds.

Hydrogenation of Santoninic Acid.—Guido Cusmano.—When sodium santoninate is hydrogenated in presence of platinum-black the product of the reaction is tetrahydrosantoninic acid, $C_{15}H_{24}O_4$. This dissolves in carbonates in the cold, gives no coloration with alcoholic potash, and has not the bitter taste of santonin. It dissolves easily in concentrated hydrochloric acid, giving a greenish brown solution, and when heated in alcoholic solution with hydroxylamine hydrochloride yields an oxime.—*Atti della Reale Accademia dei Lincei*, xxii., No. 8.

THE CHEMICAL NEWS.

VOL. CVIII., No. 2808.

BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

BIRMINGHAM, 1913.

INAUGURAL ADDRESS OF THE PRESIDENT,

Sir OLIVER LODGE, D.Sc., LL.D., F.R.S., &c.

CONTINUITY.

Natura non vincitur nisi parendo.

(Concluded from p. 136).

I OBSERVE that by some critics I have been called a vitalist, and in a sense I am; but I am not a vitalist if vitalism means an appeal to an undefined "vital force" (an objectionable term I have never thought of using) as against the laws of Chemistry and Physics. Those laws must be supplemented, but need by no means be superseded. The business of science is to trace out their mode of action everywhere, as far and as fully as possible; and it is a true instinct which resents the mediæval practice of freely introducing spiritual and unknown causes into working science. In science an appeal to occult qualities must be illegitimate, and be a barrier to experiment and research generally; as, when anything is called an Act of God—and when no more is said. The occurrence is left unexplained. As an ultimate statement such a phrase may be not only true but universal in its application. But there are always proximate explanations which may be looked for and discovered with patience. So, lightning, earthquakes, and other portents are reduced to natural causes. No ultimate explanation is ever attained by science; proximate explanations only. They are what it exists for; and it is the business of scientific men to seek them.

To attribute the rise of sap to vital force would be absurd, it would be giving up the problem and stating nothing at all. The way in which osmosis acts to produce the remarkable and surprising effect is discoverable and has been discovered.

So it is always in science, and its progress began when unknown causes were eliminated and treated as non-existent. Those causes, so far as they exist, must establish their footing by direct investigation and research; carried on in the first instance apart from the long recognised branches of science, until the time when they too have become sufficiently definite to be entitled to be called scientific. Outlandish Territories may in time be incorporated as States, but they must make their claim good and become civilised first.

It is well for people to understand this definite limitation of scope quite clearly, else they wrest the splendid work of biologists to their own confusion,—helped it is true by a few of the more robust or less responsible theorisers, among those who should be better informed and more carefully critical in their philosophising utterances.

But, as is well known, there are more than a few biologists who, when taking a broad survey of their subject, clearly perceive and teach that before all the actions of live things are fully explained, some hitherto excluded causes must be postulated. Ever since the time of J. R. Mayer it has been becoming more and more certain that, as regards performance of work, a living thing obeys the laws of physics, like everything else; but undoubtedly it initiates processes and produces results that without it could not have occurred,—from a bird's nest to a honey-comb, from a deal box to a warship. The behaviour of a ship firing shot and shell is explicable in terms of energy, but the discrimination which it exercises between friend and foe is not so explicable. There is plenty of physics and chemistry and mechanics about every vital action, but for a complete understanding of it something beyond physics and chemistry is needed.

And life introduces an incalculable element. The vagaries of a fire or a cyclone could all be predicted by Laplace's Calculator, given the initial positions, velocities, and the law of acceleration of the molecules; but no mathematician could calculate the orbit of a common house-fly. A physicist into whose galvanometer a spider had crept would be liable to get phenomena of a kind quite inexplicable, until he discovered the supernatural, *i.e.*, literally superphysical, cause. I will risk the assertion that Life introduces something incalculable and purposeful amid the laws of physics; it thus distinctly supplements those laws, though it leaves them otherwise precisely as they were and obeys them all.

We see only its effect, we do not see Life itself. Conversion of Inorganic into Organic is effected always by living organisms. The conversion under those conditions certainly occurs, and the process may be studied. Life appears necessary to the conversion; which clearly takes place under the guidance of life, though in itself it is a physical and chemical process. Many laboratory conversions take place under the guidance of life, and, but for the experimenter, would not have occurred.

Again, putrefaction, and fermentation, and purification of rivers, and disease, are not purely and solely chemical processes. Chemical processes they are, but they are initiated and conducted by living organisms. Just when medicine is becoming biological, and when the hope of making the tropical belt of the earth healthily habitable by energetic races is attracting the attention of people of power, philosophising biologists should not attempt to give their science away to Chemistry and Physics. Sections D and H and I and K are not really subservient to A and B. Biology is an independent science, and it is served, not dominated, by Chemistry and Physics.

Scientific men are hostile to superstition, and rightly so, for a great many popular superstitions are both annoying and contemptible; yet occasionally the term may be wrongly applied to practices of which the theory is unknown. To a superficial observer some of the practices of biologists themselves must appear grossly superstitious. To combat malaria Sir Ronald Ross does not indeed erect an altar; no, he oils a pond,—making libation to its presiding genii. What can be more ludicrous than the curious and evidently savage ritual, insisted on by United States Officers, at that hygienically splendid achievement the Panama Canal,—the ritual of punching a hole in every discarded tin, with the object of keeping off disease! What more absurd, again,—in superficial appearance—than the practice of burning or poisoning a soil to make it extra fertile!

Biologists in their proper field are splendid, and their work arouses keen interest and enthusiasm in all whom they guide into their domain. Most of them do their work by intense concentration, by narrowing down their scope, not by taking a wide survey or a comprehensive grasp. Suggestions of broader views and outlying fields of knowledge seem foreign to the intense worker, and he resents them. For his own purpose he wishes to ignore them, and practically he may be quite right. The folly of negation is not his, but belongs to those who misinterpret or misapply his utterances, and take him as a guide in a region where, for the time at least, he is a stranger. Not by such aid is the universe in its broader aspects to be apprehended. If people in general were better acquainted with science they would not make these mistakes. They would realise both the learning and the limitations, make use of the one and allow for the other, and not take the recipe of a practical worker for a formula wherewith to interpret the Universe.

What appears to be quite certain is that there can be no

terrestrial manifestation of life without matter. Hence naturally they say, or they approve such sayings as, "I discern in matter the promise and potency of all forms of life." Of all terrestrial manifestations of life, certainly. How else could it manifest itself save through matter? "I detect nothing in the organism but the laws of Chemistry and Physics," it is said. Very well: naturally enough. That is what they are after; they are studying the physical and chemical aspects or manifestations of life. But life itself—life and mind and consciousness—they are not studying, and they exclude them from their purview. Matter is what appeals to our senses here and now; Materialism is appropriate to the material world; not as a philosophy but as a working creed, as a proximate and immediate formula for guiding research. Everything beyond that belongs to another region, and must be reached by other methods. To explain the Psychical in terms of Physics and Chemistry is simply impossible; hence there is a tendency to deny its existence, save as an epiphenomenon. But all such philosophising is unjustified, and is really bad Metaphysics.

So if ever in their enthusiasm scientific workers go too far and say that the things they exclude from study have no existence in the universe, we must appeal against them to direct experience. We ourselves are alive, we possess life and mind and consciousness, we have first-hand experience of these things quite apart from laboratory experiments. They belong to the common knowledge of the race. Births, deaths, and marriages are not affairs of the biologist, but of humanity; they went on before a single one of them was understood, before a vestige of science existed. We ourselves are the laboratory in which men of science, psychologists, and others, make experiments. They can formulate our processes of digestion, and the material concomitants of willing, of sensation, of thinking; but the hidden guiding entities they do not touch.

So also if any philosopher tells you that you do not exist, or that the external world does not exist, or that you are an automaton without free will, that all your actions are determined by outside causes, and that you are not responsible,—or that a body cannot move out of its place, or that Achilles cannot catch a tortoise—then in all those cases appeal must be made to twelve average men, unsophisticated by special studies. There is always a danger of error in interpreting experience, or in drawing inferences from it; but in a matter of bare fact, based on our own first-hand experience, we are able to give a verdict. We may be mistaken as to the nature of what we see. Stars may look to us like bright specks in a dome, but the fact that we see them admits of no doubt. So also Consciousness and Will are realities of which we are directly aware, just as directly as we are of motion and force, just as clearly as we apprehend the philosophising utterances of an Agnostic. The process of seeing, the plain man does not understand; he does not recognise that it is a method of etherial telegraphy; he knows nothing of the ether and its ripples, nor of the retina and its rods and cones, nor of nerve and brain processes; but he sees and he hears and he touches, and he wills and he thinks and is conscious. This is not an appeal to the mob as against the philosopher, it is appeal to the experience of untold ages as against the studies of a generation.

How consciousness became associated with matter, how life exerts guidance over chemical and physical forces, how mechanical motions are translated into sensations—all these things are puzzling and demand long study. But the fact that these things are so admits of no doubt; and difficulty of explanation is no argument against them. The blind man restored to sight had no opinion as to how he was healed, nor could he vouch for the moral character of the Healer, but he plainly knew that whereas he was blind now he saw. About that fact he was the best possible judge. So it is also with "this main miracle that thou art thou, With power on thine own act and on the world."

But although Life and Mind may be excluded from Physiology, they are not excluded from Science. Of course not. It is not reasonable to say that things necessarily elude investigation merely because we do not knock against them. Yet the mistake is sometimes made. The ether makes no appeal to sense, therefore some are beginning to say that it does not exist. Mind is occasionally put into the same predicament. Life is not detected in the laboratory, save in its physical and chemical manifestations; but we may have to admit that it guides processes nevertheless. It may be called a catalytic agent.

To understand the action of life itself, the simplest plan is not to think of a microscopic organism, or any unfamiliar animal, but to make use of our own experience as living beings. Any positive instance serves to stem a comprehensive denial, and if the reality of mind and guidance and plan is denied because they make no appeal to sense, then think how the world would appear to an observer to whom the existence of men was unknown and undiscoverable, while yet all the laws and activities of nature went on as they do now.

Suppose, then, that *man* made no appeal to the senses of an observer of this planet. Suppose an outside observer could see all the events occurring in the world, save only that he could not see animals or men. He would describe what he saw much as we have to describe the activities initiated by life.

If he looked at the Firth of Forth, for instance, he would see piers arising in the water, beginning to sprout, reaching across in strange manner till they actually join or are joined by pieces attracted up from below to complete the circuit (a solid circuit round the current). He would see a sort of bridge or filament thus constructed, from one shore to the other, and across this bridge insect-like things crawling and returning for no very obvious reason.

Or let him look at the Nile, and recognise the meritorious character of that river in promoting the growth of vegetation in the desert. Then let him see a kind of untoward crystallisation growing across and beginning to dam the beneficent stream. Blocks fly to their places by some kind of polar forces; "we cannot doubt" that it is by helio- or other tropism. There is no need to go outside the laws of mechanics and physics, there is no difficulty about supply of energy—none whatever—materials in tin cans are consumed which amply account for all the energy; and all the laws of physics are obeyed. The absence of any design, too, is manifest; for the effect of the structure is to flood an area up-stream which might have been useful, and to submerge a structure of some beauty; while down stream its effect is likely to be worse, for it would block the course of the river and waste it on the desert, were it not that fortunately some leaks develop and a sufficient supply still goes down—goes down in fact more equably than before; so that the ultimate result is beneficial to vegetation, and simulates intention.

If told concerning either of these structures that an engineer, a designer in London, called Benjamin Baker, had anything to do with it, the idea would be preposterous. One conclusive argument is final against such a superstitious hypothesis—he is not there, and a thing plainly cannot act where it is not. But although we, with our greater advantages, perceive that the right solution for such an observer would be the recognition of some unknown agency or agent, it must be admitted that an explanation in terms of a vague entity called vital force would be useless, and might be so worded as to be misleading; whereas a statement in terms of mechanics and physics could be clear and definite and true as far as it went, though it must necessarily be incomplete.

And note that what we observe, in such understood cases, is an *Interaction* of Mind and Matter; not Parallelism nor Epiphenomenalism nor anything strained or difficult, but a straightforward utilisation of the properties of matter and energy for purposes conceived in the mind, and executed by muscles guided by acts of will.

But, it will be said, this is unfair, for we *know*

there is design in the Forth Bridge or the Nile Dam, we have seen the plans and understand the agencies at work; we know that it was conceived and guided by life and mind, it is unfair to quote this as though it could simulate an automatic process.

Not at all, say the extreme school of biologists whom I am criticising, or ought to say if they were consistent, there is nothing but Chemistry and Physics at work anywhere; and the mental activity apparently demonstrated by those structures is only an illusion, an epiphenomenon; the laws of chemistry and physics are supreme, and they are sufficient to account for everything!

Well, they account for things up to a point; they account in part for the colour of a sunset, for the majesty of a mountain peak, for the glory of animate existence. But do they account for everything completely? Do they account for our own feeling of joy and exultation, for our sense of beauty, for the manifest beauty existing throughout nature? Do not these things suggest something higher and nobler and more joyous, something for the sake of which all the struggle for existence goes on?

Surely there must be a deeper meaning involved in natural objects. Orthodox explanations are only partial, though true as far as they go. When we examine each particoloured pinnule in a peacock's tail, or hair in a zebra's hide, and realise that the varying shades on each are so placed as to contribute to the general design and pattern, it becomes exceedingly difficult to explain how this organised co-operation of parts, this harmonious distribution of pigment cells, has come about on merely mechanical principles. It would be as easy to explain the sprouting of the cantilevers of the Forth Bridge from its piers, or the flocking of the stones of the Nile Dam by chemiotaxis. Flowers attract insects for fertilisation; and fruit tempts animals to eat it in order to carry seeds. But these explanations cannot be final. We have still to explain the insects. So much beauty cannot be necessary merely to attract their attention. We have further to explain this competitive striving towards life. Why do things struggle to exist? Surely the effort must have some significance, the development some aim. We thus reach the problem of Existence itself, and the meaning of Evolution.

The mechanism whereby existence entrenches itself is manifest, or at least has been to a large extent discovered. Natural Selection is a vera causa, so far as it goes; but if so much beauty is necessary for insects, what about the beauty of a landscape or of clouds? What utilitarian object do those subserve? Beauty in general is not taken into account by science. Very well, that may be all right, but it exists nevertheless. It is not my function to discuss it. No; but it is my function to remind you and myself that our studies do not exhaust the universe, and that if we dogmatise in a negative direction, and say that we can reduce everything to physics and chemistry, we gibbet ourselves as ludicrously narrow pedants, and are falling far short of the richness and fullness of our human birthright. How far preferable is the reverent attitude of the Eastern Poet:—

> "The world with eyes bent upon thy feet stands in awe with all its silent stars."

Superficially and physically we are very limited. Our sense organs are adapted to the observation of matter; and nothing else directly appeals to us. Our nerve-muscle system is adapted to the production of motion in matter, in desired ways; and nothing else in the material world can we accomplish. Our brain and nerve systems connect us with the rest of the physical world. Our senses give us information about the movements and arrangements of matter. Our muscles enable us to produce changes in those distributions. That is our equipment for human life; and human history is a record of what we have done with these parsimonious privileges.

Our brain, which by some means yet to be discovered connects us with the rest of the material world, has been thought partially to disconnect us from the mental and spiritual realm, to which we really belong but from which for a time and for practical purposes we are isolated. Our common or social association with matter gives us certain opportunities and facilities, combined with obstacles and difficulties which are themselves opportunities for struggle and effort.

Through matter we become aware of each other, and can communicate with those of our fellows who have ideas sufficiently like our own for them to be stimulated into activity by a merely physical process set in action by ourselves. By a timed succession of vibratory movements (as in speech and music), or by a static distribution of materials (as in writing, painting, and sculpture), we can carry on intelligent intercourse with our fellows; and we get so used to these ingenious and roundabout methods, that we are apt to think of them and their like as not only the natural but as the only possible modes of communication, and that everything more direct would disarrange the whole fabric of science.

It is clearly true that our bodies constitute the normal means of manifesting ourselves to each other while on the planet; and that if the physiological mechanism whereby we accomplish material acts is injured, the conveyance of our meaning and the display of our personality inevitably and correspondingly suffer.

So conspicuously is this the case that it has been possible to suppose that the communicating mechanism, formed and worked by us, is the whole of our existence; and that we are essentially nothing but the machinery by which we are known. We find the machinery utilising nothing but well-known forms of energy, and subject to all the laws of chemistry and physics—it would be strange if it were not so—and from that fact we try to draw valid deductions as to our nature, and as to the impossibility of our existing apart from and independent of these temporary modes of material activity and manifestation. We so uniformly employ them, in our present circumstances, that we should be on our guard against deception due to this very uniformity. Material bodies are all that we have any control over, are all that we are experimentally aware of; anything that we can do with these is open to us; any conclusions we can draw about them may be legitimate and true. But to step outside their province and to deny the existence of any other region because we have no sense organ for its appreciation, or because (like the Ether) it is too uniformly omnipresent for our ken, is to wrest our advantages and privileges from their proper use and apply them to our own misdirection.

But if we have learnt from science that Evolution is real, we have learnt a great deal. I must not venture to philosophise, but certainly from the point of view of science Evolution is a great reality. Surely evolution is not an illusion; surely the universe progresses in time. Time and Space and Matter are abstractions, but are none the less real: they are data given by experience; and Time is the keystone of evolution. "Thy centuries follow each other, perfecting a small wild flower."

We abstract from living moving Reality a certain static aspect, and we call it Matter; we abstract the element of progressiveness, and we call it Time. When these two abstractions combine, co-operate, interact, we get reality again. It is like Poynting's theorem.

The only way to refute or confuse the theory of Evolution is to introduce the subjectivity of time. That theory involves the reality of time, and it is in this sense that Prof. Bergson uses the great phrase "Creative Evolution."

I see the whole of material existence as a steady passage from past to future, only the single instant which we call the present being actual. The past is not non-existent, however, it is stored in our memories, there is a record of it in matter, and the present is based upon it; the future is the outcome of the present, and is the product of evolution.

Existence is like the output from a loom. The pattern, the design for the weaving, is in some sort "there" already;

but whereas our looms are mere machines, once the guiding cards have been fed into them, the Loom of Time is complicated by a multitude of free agents who can modify the web, making the product more beautiful or more ugly according as they are in harmony or disharmony with the general scheme. I venture to maintain that manifest imperfections are thus accounted for, and that *freedom* could be given on no other terms, nor at any less cost.

The ability thus to work for weal or woe is no illusion, it is a reality, a responsible power which conscious agents possess; wherefore the resulting fabric is not something preordained and inexorable, though by wide knowledge of character it may be inferred. Nothing is inexorable except the uniform progress of time; the cloth must be woven, but the pattern is not wholly fixed and mechanically calculable.

Where inorganic matter alone is concerned, there everything is determined. Wherever full consciousness has entered, new powers arise, and the faculties and desires of the conscious parts of the scheme have an effect upon the whole. It is not guided from outside but from within; and the guiding power is immanent at every instant. Of this guiding power we are a small but not wholly insignificant portion.

That evolutionary progress is real is a doctrine of profound significance, and our efforts at social betterment are justified because we are a part of the scheme, a part that has become conscious, a part that realises, dimly at any rate, what it is doing and what it is aiming at. Planning and aiming are therefore not absent from the whole, for we are a part of the whole, and are conscious of them in ourselves.

Either we are immortal beings or we are not. We may not know our destiny, but we must have a destiny of some sort. Those who make denials are just as likely to be wrong as those who make assertions; in fact, denials are assertions thrown into negative form. Scientific men are looked up to as authorities, and should be careful not to mislead. Science may not be able to reveal human destiny, but it certainly should not obscure it. Things are as they are, whether we find them out or not; and if we make rash and false statements, posterity will detect us—if posterity ever troubles its head about us. I am one of those who think that the methods of Science are not so limited in their scope as has been thought; that they can be applied much more widely, and that the Psychic region can be studied and brought under law too. Allow us anyhow to make the attempt. Give us a fair field. Let those who prefer the materialistic hypothesis by all means develop their thesis as far as they can; but let us try what we can do in the Psychical region, and see which wins. Our methods are really the same as theirs—the subject-matter differs. Neither should abuse the other for making the attempt.

Whether such things as intuition and revelation ever occur is an open question. There are some who have reason to say that they do. They are at any rate not to be denied off-hand. In fact, it is always extremely difficult to deny *anything* of a general character, since evidence in its favour may be only hidden and not forthcoming, especially not forthcoming at any particular age of the world's history, or at any particular stage of individual mental development. Mysticism must have its place, though its relation to Science has so far not been found. They have appeared disparate and disconnected, but there need be no hostility between them. Every kind of reality must be ascertained and dealt with by proper methods. If the voices of Socrates and of Joan of Arc represent real psychical experiences, they must belong to the intelligible universe.

Although I am speaking ex cathedra, as one of the representatives of orthodox science, I will not shrink from a personal note summarising the result on my own mind of thirty years' experience of psychical research, begun without predilection—indeed with the usual hostile prejudice. This is not the place to enter into details or to discuss facts scorned by orthodox science, but I cannot help remembering that an utterance from this Chair is no ephemeral production, for it remains to be criticised by generations yet unborn, whose knowledge must inevitably be fuller and wider than our own. Your President therefore should not be completely bound by the shackles of present-day orthodoxy, nor limited to beliefs fashionable at the time. In justice to myself and my co-workers I must risk annoying my present hearers, not only by leaving on record our conviction that occurrences now regarded as occult can be examined and reduced to order by the methods of science carefully and persistently applied, but by going further and saying, with the utmost brevity, that already the facts so examined have convinced me that memory and affection are not limited to that association with matter by which alone they can manifest themselves here and now, and that personality persists beyond bodily death. The evidence to my mind goes to prove that discarnate intelligence, under certain conditions, may interact with us on the material side, thus indirectly coming within our scientific ken; and that gradually we may hope to attain some understanding of the nature of a larger, perhaps etherial, existence, and of the conditions regulating intercourse across the chasm. A body of responsible investigators have even now landed on the treacherous but promising shores of a new continent.

Yes, and there is more to say than that. The methods of science are not the only way, though they are our way, of arriving at truth. "*Uno itinere non potest perveniri ad tam grande secretum.*"

Many scientific men still feel in pugnacious mood towards Theology, because of the exaggerated dogmatism which our predecessors encountered and overcame in the past. They had to struggle for freedom to find truth in their own way; but the struggle was a miserable necessity, and has left some evil effects. And one of them is this lack of sympathy, this occasional hostility, to other more spiritual forms of truth. We cannot really and seriously suppose that truth began to arrive on this planet a few centuries ago. The pre-scientific insight of genius—of Poets and Prophets and Saints—was of supreme value, and the access of those inspired seers to the heart of the universe was profound. But the camp followers, the scribes and pharisees, by whatever name they may be called, had no such insight, only a vicious or a foolish obstinacy; and the prophets of a new era were stoned.

Now at last we of the new era have been victorious; we inherit the fruits of the age-long conflict, and the stones are in our hands. Let us not fall into the old mistake of thinking that ours is the only way of exploring the multifarious depths of the universe, and that all others are worthless and mistaken. The universe is a larger thing than we have any conception of, and no one method of search will exhaust its treasures.

Men and brethren, we are trustees of the truth of the physical universe as scientifically explored; let us be faithful to our trust.

Genuine religion has its roots deep down in the heart of humanity and in the reality of things. It is not surprising that by our methods we fail to grasp it; the actions of the Deity make no appeal to any special sense, only a universal appeal; and our methods are, as we know, incompetent to detect complete uniformity. There is a Principle of Relativity here, and unless we encounter flaw or jar or change, nothing in us responds; we are deaf and blind therefore to the immanent Grandeur around us, unless we have insight enough to appreciate the Whole, and to recognise in the woven fabric of existence, flowing steadily from the loom in an infinite progress towards perfection, the ever-growing garment of a transcendent God.

Summary of the Argument.

A marked feature of the present scientific era is the discovery of, and interest in, various kinds of Atomism; so that Continuity seems in danger of being lost sight of.

Another tendency is toward comprehensive negative generalisations from a limited point of view.

Another is to take refuge in rather vague forms of statement, and to shrink from closer examination of the puzzling and the obscure.

Another is to deny the existence of anything which makes no appeal to organs of sense, and no ready response to laboratory experiment.

Against these tendencies the author contends. He urges a belief in ultimate continuity as essential to science; he regards scientific concentration as an inadequate basis for philosophic generalisation; he believes that obscure phenomena may be expressed simply if properly faced; and he points out that the non-appearance of anything perfectly uniform and omnipresent is no argument against its real substantial existence.

ADDRESS TO THE CHEMICAL SECTION OF THE BRITISH ASSOCIATION.

Birmingham, 1913.

By Prof. W. P. Wynne, D.Sc., F.R.S., President of the Section.

When the present position of education in Birmingham is considered, the transformation effected since the 'seventies is little short of marvellous. Five-and-thirty years ago, when I became an evening student, classes conducted by the Midland Institute met the demand for Arts and Science subjects; now a University—venerable in comparison with all Civic Universities save the Victoria University of Manchester—exists to provide instruction in every branch of learning. The spacious building in which we meet—already too small for the demands made on it—is the lineal descendant of that part of the Midland Institute which formerly was used for evening class instruction in science, organised in connection with the Science and Art Department, and financed largely by the system of payment on results; this large lecture theatre replaces the small and inconvenient classroom in which the teaching of Chemistry and Physics under Mr. Woodward was carried on. Payment on results is obsolete, and the "May" examinations on which it was based have almost disappeared, assessment by inspection now replacing both; nevertheless, it is more than doubtful whether any other system—in the circumstances of the time—could have spread so widely a knowledge of science among the people, or prepared the way for the Technical Instruction Act, and that appreciation of the value of scientific training for industrial pursuits, which is exemplified by the provision through municipal agencies of Technical Schools in the industrial centres of this country. I sometimes think the Science and Art Department, and those great men, Sir John Donnelly and Professor Huxley, who did much to shape its attitude towards science instruction in evening classes and in the Science Schools at South Kensington (Note 1), have received something less than their share of credit for pioneering work which finds its fruition in well-equipped Institutions like this, and in the enhanced position which science holds to-day in the estimation of our countrymen. In those far-off times, before the foundation stone of Mason College was laid, such evening classes in Birmingham provided the only means by which instruction in science, or scholarships to South Kensington, could be obtained. It is not unfitting, therefore, that I—a product of the system—should acknowledge here the obligation under which I stand both to the Midland Institute and to the Science and Art Department for providing the ladder by which I have risen, however undeservedly, to the honourable position of President of this Section.

The historian of our times will not fail to note some of the consequences which have followed the application of science to industry, possibly also some of the educational results which have followed the development of science teaching in schools of all grades. Except from one point of view these need not concern us now as they fall, the one in so far as Chemistry is concerned, into the province of the Society of Chemical Industry, the other mainly within the purview of Section L. This bringing of Chemistry to the people has aroused a widespread interest in some aspects of the subject, of which the Press has not been slow to take note. Not even the heuristic method can hide from the schoolboy the fact that certain fundamental conceptions are accepted which do not admit of proof, such as the indivisible atom, the non-decomposable element, the indestructibility of matter. When therefore, as one of the first-fruits of his discovery that positive rays furnish the most delicate method of chemical analysis, Sir J. J. Thomson has obtained from the most diverse solids a new gas, X_3; and by a different procedure, Professor Collie with Mr. Patterson have discovered that hydrogen, under the influence of electric discharges at low pressure, becomes replaced by neon, helium, and a third gas which is possibly identical with X_3 (Note 2), it is not surprising that we should hear much about it in the newspapers, just as was the case when the disintegration of radium was in process of being established. Further investigation may fail to substantiate some of the views which have been expressed about this unexplained disappearance of hydrogen; the origin of the neon and helium which make their appearance in the tube as the experiments proceed; the source of the gas X_3. Fortunately X_3, unlike neon and helium, has some chemical properties—it disappears, for example, when violently exploded with a mixture of oxygen and hydrogen (Note 3)—but we do not yet know whether it is a new element with an atomic weight of about 3, or a compound of hydrogen with an element yet to be discovered. This much at least seems certain: it is not the gas which, according to Mendeleeff, should precede fluorine in the halogen series, but whether its discovery, like that of argon, will necessitate a revision of the Periodic Table of the elements we cannot know until the mystery which at present surrounds it has been dispelled.

It was in 1886, at the last meeting of this Association in Birmingham, that Sir William Crookes - whose continued activities are a source of pride and gratification to his brother chemists—gave that famous Address in which, clothing his ideas in language which has something of the magic of word-painting, he traced the evolution of the elements, as we know them, from the hypothetical protyle or Urstoff. The common origin of all elementary substances is now an accepted theory, although the question whether the idea underlying the term "transmutation" is verifiable under available conditions is answered differently according to the view we take of the disintegration of radium and kindred phenomena. But no one could have imagined that before another Birmingham meeting, the Periodic Table to which Sir William Crookes devoted much attention would have been enriched not only by a series or elements devoid of chemical properties, but by a second series, known only in minute quantities, and displaying those extraordinary properties of radio-activity which have revolutionised our ideas in more than one direction.

It is not necessary for me to chronicle even the more striking achievements in chemistry since 1886; a few examples will show how great the progress has been. It is on record that Arrhenius was present at that meeting, but his advocacy of that theory of solutions with which his name will always be associated came a little later; phenylhydrazine, which was to play so important a part in Emil Fischer's investigation of the sugars, had been discovered by him only two years previously; the Grignard reagent, which in other directions has played a no less important part in synthetical organic chemistry, did not become available until some fourteen years later. Theories then emerging, such as that of geometrical isomerism, have

either been discarded or modified by the discovery of new facts, and who shall say that the ionic theory of dissociation stands where it did, now that ions in solution have incurred the suspicion of associating with the solvent, and to that extent have come into line with molecules, for the orthodox behaviour of which Professor Armstrong himself would no doubt be prepared to vouch.

Residual Valency.

Among the many doctrines which have suffered under the stress of long sustained investigation, that of valency is a prominent example. Valency is that property by which an atom attracts to itself other atoms or radicals, and its numerical value is deduced from the structural formulæ of compounds in which that atom occurs. Claus seems to have been the first to recognise that this attraction between two atoms is not a constant, but depends on the nature of the other atoms or radicals in the molecule (Note 4), and it is of interest to note in connection with what follows that he used methane and its chloro-derivatives to illustrate his point of view. Valency may vary, therefore, from compound to compound; it is known to alter under the influence of change in temperature, as, for example, when carbon dioxide or phosphorus pentachloride undergoes thermal dissociation. But Claus's view did not meet with ready acceptance; hence at the Birmingham Meeting few chemists, if any, would have questioned the quadrivalency of carbon, despite the difficulty caused by the existence of carbon monoxide. Now, carbon is believed to be bivalent in the carbamines, fulminic acid and other compounds as well as in carbon monoxide, and its tervalency is coming to be accepted in the light of the latest investigations on triphenylmethyl and its congeners. What is true of carbon is equally true of all other elements, except argon and its companions. Hence the doctrine of constant valency for which Kekulé contended, or that of variable valency in which the uncombined units varied by even numbers has necessarily given place to one of less rigid type, although the final form has yet to be determined.

For the purpose of this Address it will be sufficient to refer only to one of these later theories: that in which Werner, as the outcome of his exhaustive study of inorganic molecular compounds, and especially of the ammines, supposes that an atom may have both principal and auxiliary or residual valency (Note 5). There are difficulties in its application to certain problems of organic chemistry—for example, the structure of the benzene molecule—but the conspicuous success which has attended Werner's investigation of the complicated isomerism of the cobalt and chromium ammines is evidence of its value as a guide in stimulating research in the most unpromising directions (Note 6). Werner's view that valency is an attractive force acting from the centre of the atom, being of equal value at all points on the surface and independent of units of affinity, has the merit of meeting the objection long urged to the idea that affinity has fixed direction in space, but otherwise leaves untouched van't Hoff's brilliant conception of asymmetry which plays so great a part in the chemistry of to-day.

What light does this conception of residual valency, dating back to 1885, if not earlier (Note 7), and now embodied in many theories besides Werner's, throw on some of the problems with which the organic chemist is faced? Much every way. The question of the distribution of valency in the molecules of carbon compounds is discussed probably more than any other; it arises in connection with the structure of unsaturated compounds, the properties of fluorescence or colour which many of them exhibit, and the relation between chemical constitution and physical properties, to the elucidation of which an increasing amount of research is being directed. The double linkings in our formulæ no longer represent two units of valency in terms of hydrogen, nor are they now used to indicate polarity of the central atom or distribution of the valency in space; Werner's conception of valency accounts, as the phase goes, for the concentration of residual activity at that part of the molecule where unsaturation exists, and it is of service when different degrees of unsaturatedness are displayed by compounds which, on the older view, would be expected to show similarity in chemical behaviour (Note 8). With your permission I propose briefly to review our knowledge of that type of chemical change known as substitution from the standpoint of residual valency.

Substitution in the Paraffin Series.

So far back as 1839 the fact was discovered that replacement of hydrogen by chlorine in the acetic acid molecule does not lead to any essential modification in the properties of the acid. It is not a little remarkable therefore that although much of the progress in organic chemistry has been achieved by substitutions of the most diverse types, we are still unable to say that agreement has been reached with regard to the nature of the processes by which this replacement of one radical by another in a molecule is brought about. Never has attention been concentrated more closely than now on the study of what, for want of a better phrase, is termed the "mechanism of chemical reactions"—the processes which are covered and hidden by the sign of equality used, inaptly, in chemical equations—but the integrating mind, to the need for which Professor Frankland alluded on a recent occasion (Note 9), has not yet been evolved to reconcile the uncertain or contradictory answers vouchsafed to much patient experimenting. Organic chemistry is not singular in this respect; as much might be said about controversies not yet settled which concern themselves with such every-day phenomena as the chemistry of the candle-flame or of the rusting of iron.

It is a commonplace that Kekulé, to whom theoretical chemistry owes so many fruitful suggestions, was of the opinion that substitution is not a process in which what may be called a direct exchange of radicals occurs, but is preceded by the temporary union of the molecules of carbon compound and addendum, followed by disruption into two new molecules, the substituted carbon compound being one of them. It is clear, then, from the standpoint of Kekulé's hypothesis, that some degree of unsaturation is to be looked for in all carbon compounds and in all addenda. Hence, the paraffin hydrocarbons which furnish derivatives only by substitution, and under the older, more rigid view of valency propounded by Kekulé himself, are typically saturated compounds, supply the exceptions to prove the general validity of the hypothesis that addition precedes substitution.

Before examining the case of these hydrocarbons, however, some advantage may be gained if the behaviour of other groups of compounds be examined in the light of the idea underlying Kekulé's view. By reference to the literature, it is evident that since the beginning of this century attention has been concentrated on the phenomena of substitution in the important group of carbonyl compounds, particularly the ketones and acids, which in many cases yield halogen substitution derivatives of one type. Thus methyl ethyl ketone when brominated in sunlight yields two bromoketobutanes of the constitution shown in the following formulæ, and propionic acid with bromine and red phosphorus under Volhard's conditions (Note 10) gives α-bromopropionic acid,—

$CH_2Br{\cdot}CO{\cdot}CH_2{\cdot}CH_3$ and $CH_3{\cdot}CO{\cdot}CHBr{\cdot}CH_3$ (Note 11)

$CH_3{\cdot}CHBr{\cdot}CO{\cdot}OH$,

the halogen occupying what is termed the α-position with reference to the carbonyl radical. Why is substitution easier in the methyl group when it is present in the ketone or acid than when it occurs in methane, is one question that may be asked. A second will inquire whether the carbonyl group has a directing influence, and, if so, by what means is it exercised.

It has been supposed by Werner that the distribution of valency is disturbed by the introduction of the oxygen atom of the carbonyl group into the molecule of the hydro-

carbon; that this oxygen atom absorbs much of the valency of the carbon atom of the carbonyl group, leaving less to bind its neighbour or neighbours, which results in their having free valency, and thereby attaching substituents to themselves. This explanation, if accepted for the bromination of ketones and acids, also for the chlorination of ketones, does not account for the results recorded by Michael and by Montemartini in the case of carboxylic acids. Michael has found that the β-chloro, not the α-chloro, acid is the chief product (60—65 per cent) when homologues of acetic acid are chlorinated (Note 12); and Montemartini states that if the radical CH occur in any part of the carbon chain the exchange of hydrogen for chlorine takes place in that position, however distant it may be from the carbonyl group of the acid (Note 13).

$$CH_3{\cdot}CH_2{\cdot}CHCl{\cdot}CH_2{\cdot}CO{\cdot}OH$$
(Michael)

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!>CCl{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}OH.$$
(Montemartini)

At present there seems to be no clue to the reason why chlorine and bromine in these reactions behave alike towards ketones and not towards acids.

An alternative explanation of this reaction, which has come to be widely accepted, is based on the remarkable property called desmotropy or dynamic isomerism, which certain of these carbonyl compounds exhibit. A desmotropic compound may exist in two or more forms, and its peculiar isomerism is known to depend on the mobility of a hydrogen atom in the complex $\cdot CH_2{\cdot}CO\cdot$ whereby an equilibrium is set up of the type:—

$$\underset{\text{Ketonic form}}{\cdot CH_2{\cdot}CO\cdot} \rightleftharpoons \underset{\text{Enolic form}}{\cdot CH{:}C(OH)\cdot}$$

Of these two forms, the enolic is the more unsaturated, and presumably the more reactive (Note 14). Lapworth, making use of this desmotropic relationship, supposes that when the ketone reacts with halogen in dilute aqueous solution three changes occur which, for the case of acetone, may be represented by the following expressions:—

$$CH_3{\cdot}CO{\cdot}CH_3 \rightarrow CH_3{\cdot}C(OH){:}CH_2$$
$$CH_3{\cdot}C(OH){:}CH_2+Br_2 \rightarrow CH_3{\cdot}C(OH)Br{\cdot}CH_2Br.$$
$$CH_3{\cdot}C(OH)Br{\cdot}CH_2Br \rightarrow CH_3{\cdot}CO{\cdot}CH_2Br+HBr$$

the first being one of slow enolisation, accelerated catalytically by halogen acid, leading to the production of an unsaturated compound, which then by rapid addition of bromine and subsequent elimination of hydrogen bromide conforms with Kekulé's hypothesis. The intermediate compounds, it is true, have not been isolated, but a study of the dynamics of the reaction by Lapworth, and later by Dawson with his collaborators (using iodine instead of bromine), shows that this explanation is in harmony with the data obtained (Note 15). When the reaction is applied to carboxylic acids under similar conditions, the view that it takes a similar course finds support from an investigation of the dynamics of the bromination of malonic acid in aqueous solution (Note 16).

Whether evidence drawn from reactions found to take place in aqueous solution is relevant when bromination is effected by heating a carboxylic acid with bromine and red phosphorus may be doubted. Certainly it seems to afford no assistance in accounting for the course of chlorination in the acids examined by Michael and by Montemartini. Nevertheless, Aschan employs the keto-enolic hypothesis (Note 17) to elucidate the results of a recent inquiry into the "mechanism" of the Volhard reaction (Note 18); and it may be added that racemisation has been found to occur when *lævo*-valeric acid is brominated by Volhard's method (Note 19)—a result which must follow if enolisation take place, although susceptible of another explanation.

So far as I can form a judgment, no case has been made out for the view that substitution of halogen for hydrogen under Volhard's conditions differs in its "mechanism" from substitution in the paraffins. This opinion finds support in the discovery just announced by Leuchs (Note 20) that, while the chief product of the bromination of *dextro*-β-carboxybenzyl-α-hydrindone—

$$C_6H_4\!<\!\begin{matrix}CH_2\\CO\end{matrix}\!>\!CH{\cdot}CH_2{\cdot}C_6H_4{\cdot}CO_2H \rightarrow C_6H_4\!<\!\begin{matrix}CH_2\\CO\end{matrix}\!>\!CBr{\cdot}CH_2{\cdot}C_6H_4{\cdot}CO_2H$$

is the racemic compound, no less than 10 per cent is the *dextro*-bromo-derivative; therefore, the inference is clear that in the formation of the latter compound, if not of both, substitution was effected by a process in which migration of the hydrogen atom did not occur.

Attention may now be directed to the question of "direct substitution," which, in its simplest form, is encountered in the paraffin series. As will be gathered from the following selection from among the various theories propounded to account for the mechanism of substitution, alternative explanations of the intermediate reactions leading up to substitution in these cases involve either elimination of the hydrogen atom before introduction of the halogen, or addition of the halogen in virtue of the supposed residual valency of both molecules, followed by disruption of the complex thus formed into the known products of the change.

Dealing with these alternatives in the order given, Arrhenius adopts a view of the process of substitution, which, including as it does his explanation of optical inversion and racemisation, should perhaps be given in his own words:—

"Every valency linking can be broken; this is true in all cases, since it is a necessary condition for every chemical reaction. An atom or an atomic complex is thereby removed from the molecule, and its place taken by another atom or atomic complex. One must therefore assume, as was first pointed out by Williamson, that the atoms or complexes separate themselves from the molecule from time to time, even when they do not react with other molecules. Consider now a molecule in which four different atoms, A, B, C, and D, are bound to one carbon atom. The atoms A and B, which may possess equal charges, *e.g.*, positive, are therefore separated at times from the molecule, and it may happen that they are both separated at one and the same time. It is therefore possible for them to change places on combining with the carbon atom again. This is synonymous with a transformation of the original molecule into its optical isomer (Note 21).

Nef, making use of "the conception of dissociation in its broadest sense," is of opinion that the decomposition of ethane into hydrogen and ethylene at 800° "proves that an extremely small per cent of [its] molecules must exist at ordinary temperature in an active or dissociated condition,—

$$CH_3{\cdot}CH_3 \rightarrow CH_3{\cdot}CH_2+H-\text{" (Note 22),}$$

consequently, when "chlorine reacts with ethane to give the monochloro- substitution product, we have this reagent in the *active molecular* condition simply uniting by addition with the dissociated ethane particles,—

$$\begin{matrix}Cl=Cl\\ | \quad\ \ | \end{matrix} + H{-}C_2H_5 \rightarrow \begin{matrix}Cl=Cl\\ | \quad\ \ | \\ H \quad C_2H_5\end{matrix} \quad [\rightarrow HCl+C_2H_5Cl.]\text{"}$$

Finally, he draws the conclusion that "excluding reactions called ionic, a chemical reaction between two substances always first takes place by their union to form an additive compound."

Michael (Note 23), in many published papers, has emphasised the view that in the substitution of halogen for hydrogen in a saturated hydrocarbon or saturated acid the principal factors to be taken into account are the mutual chemical attraction of the two elements, on the one hand, and that of the halogen and carbon, on the other. By applying his "positive-negative" hypothesis to the directing influence of "relatively-positive" methyl, and

"relatively-negative" carboxyl, he draws conclusions about the degree of firmness or looseness with which particular hydrogen atoms are bound to carbon in the molecule, and is thereby able to forecast with some success the position or positions in which replacement of hydrogen by halogen will occur. Flürscheim, in the discussion of the relation between the strength of acids and bases, and the quantitative distribution of affinity in the molecule, also makes use of the idea that the relative degree of firmness or looseness with which a hydrogen atom is held depends on the nature of the other atoms or radicals associated with the same carbon atom (Note 24). The hydrogen atoms therefore are not to be regarded as retained in the molecule with the same degree of firmness; in other words, valency is not a constant to be measured in units.

It will be gathered, therefore, that Arrhenius and Nef, from different standpoints, support the idea that separation of hydrogen from the hydrocarbon precedes entry of the substituent into the molecule; Michael and Flürscheim are concerned chiefly with the distribution of valency in the molecule, which determines whether a particular hydrogen atom shall be displaced by hydrogen or not; Kekulé's hypothesis requires addition to precede substitution. Is there any experimental evidence to indicate where the balance of probability lies? I think it can be argued that the phenomena of substitution observed with optically active substances do not lend support to the views of Arrhenius or of Nef, which imply actual or virtual dissociation, but that they point to the intermediate formation of an additive product, which undergoes scission as Kekulé supposed. Such an additive product can be formed only if residual valencies be present in both carbon compound and addendum.

The argument runs thus:—Unless valency has fixed direction in space, a conception now abandoned if modern theories of valency be accepted, the conclusion seems to be inevitable that dissociation of the optically active compound—

$$\text{CWXYZ into } \dot{\text{C}}\text{WXY} + \text{Z},$$

must lead to racemisation, the radicals W, X, Y, distributing themselves in two-dimensional space, thus destroying the asymmetry; whence it follows that introduction of the substituent, V, into the molecule in place of Z can give rise only to an optically inactive product. Now, it is a well established fact that a radical attached directly to the asymmetric carbon atom may be replaced by another without racemisation following (Note 25). Therefore, preliminary dissociation being excluded, Kekulé's additive hypothesis remains. But the prolonged study of that remarkable reaction known as the "Walden inversion" by Emil Fischer, McKenzie, and other investigators has led to results which, if the views formed independently by Fischer (Note 26), Werner (Note 27), and Pfeiffer (Note 28) may be accepted, are inexplicable unless a preliminary addition, effected as it is supposed by means of residual valencies, precedes this replacement of the eliminated radical by the substituent.

The Walden inversion may be illustrated by a brief statement of some of the facts discovered in connection with the conversion of optically active chlorosuccinic acid into malic acid

$$\text{R}\cdot\text{CH(OH)}\cdot\text{CO}_2\text{H} \rightarrow \text{R}\cdot\text{CHCl}\cdot\text{CO}_2\text{H} \rightarrow \text{R}\cdot\text{CH(OH)}\cdot\text{CO}_2\text{H}.$$

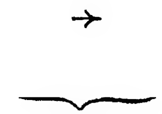
Walden found that *lævo*-chlorosuccinic acid, obtained from *dextro*-malic acid, furnished either *dextro*- or *lævo*-malic acid, according to the reagent used to effect of the replacement of the Cl by the OH radical.

$$l\text{-Chlorosuccinic acid} \begin{cases} \nearrow (+\text{Ag}_2\text{O}) \rightarrow l\text{-malic acid.} \\ \searrow (+\text{KOH}) \rightarrow d\text{-malic acid.} \end{cases}$$

And as the corresponding inversion was found to occur with *dextro* chlorosuccinic acid under similar conditions, a complete cycle of changes can be brought about (Note 29). That preservation of optical activity, and not racemisation, should accompany the replacement of a radical, attached to the asymmetric carbon atom, by another is a fact of much theoretical interest, as has already been indicated; that a change in the sign of rotation should occur when an exchange of the same radicals is achieved by one reagent and not by another is a mystery, that deepens rather than diminishes with each addition to the list of inversions, already long, in which it has been observed (Note 30). In all probability the discovery of the Walden inversion, as Prof. Frankland has said, "may mark an epoch in our views with regard to the mechanism of the process of substitution in general" (Note 31).

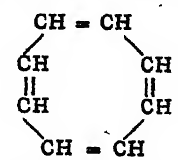
The Structure of the Benzene Molecule.

The abandonment of the theory of the fixed valency unit in favour of the view that the carbon atom has both principal and residual valencies has raised afresh that perennial topic of controversy—the structure of the benzene molecule. Probably few will contest the statement that for practical purposes only three formulæ have emerged from the long discussion of the problem, viz., Kekulé's oscillation formula with fixed valency units, for which much physical evidence has been pleaded; Thiele's formula, in which his theory of "conjugated double linkings" is applied to the Kekulé formula, with the consequence that the three double linkings disappear owing to self-neutralisation of the partial valencies, the benzene molecule thus containing six inactive double linkings (Note 32); and Armstrong's "centric" formula, in which by its residual valency "each individual carbon atom exercises an influence upon each and every other carbon atom" (Note 33). The dotted lines indicate he residual valencies.



Kekulé. Thiele. Armstrong.

The discovery of *cyclo*octatetraene has brought a new interest into the discussion (Note 34), for the structural formula assigned to this hydrocarbon shows alternate single and double linkings as in Kekulé's symbol, and the optical behaviour (refractivity) corresponds with that of benzene.



But its chemical properties are entirely different from those of benzene; it forms compounds not by substitution but by addition, and it has the reactivities of a highly unsaturated compound. If these experimental results be accepted, then—as Willstätter shows—the peculiar properties of benzene are not to be explained by Kekulé's or Thiele's formula, and the verdict is given in favour of the "centric" symbol—that earliest embodiment of the conception of residual valency, which Armstrong later turned to such good account in the quinonoid theory of colour identified with his name.

The reference to the optical behaviour of *cyclo*octatetraene may perhaps suggest the inquiry:—Do not the physical properties of the carbon compounds throw light on the questions that have been raised? A little consideration will show that, on the contrary, the answer must be:—It is only by chemical evidence that physical data can be interpreted or corroborated, and in the absence of such evidence the "additive" results which accrue from

physical observations have no bearing on questions involving the determination of structure or the structural transformations which accompany a chemical change. For example, the anomalous results obtained by Brühl and by Sir William Perkin (Note 35) in the investigation of the refractivity and the magnetic rotation of certain unsaturated compounds, remained without explanation until Thiele in 1899, by his hypothesis of partial valency, accounted for the comparative inactivity of the central pair of carbon atoms in compounds of this type—compounds which are characterised by containing alternate single and double linkings in their formulæ

·CH:CH·CH:CH· → ·CHBr·CH:CH·CHBr·

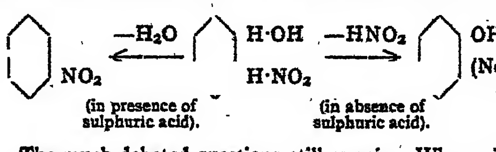
This conception of Thiele's has both focussed attention on the distribution of valency within the molecule, contributing largely to the wide acceptance of theories of valency such as Werner's, and given to the study of physical properties—especially those "constitutive" properties of refraction, dispersion, and magnetic rotation—an impetus which has by no means spent its force. Further, the occurrence of this anomaly, "exaltation" as it is called, is now relied on as evidence of the presence of this particular distribution of valency, with results which in Auwers's hands have furnished important clues to the structural formulæ of terpenes and other compounds.

As additive properties become constitutive, so the value of a knowledge of the physical properties of a substance will tend to increase, but there is little ground for hope that the problem of the constitution of benzene will be solved from the physical side. The controversy which has arisen between Hantzsch and Auwers regarding the physical properties of *cyclo*octatetraene in relation to its chemical structure is a case in point (Note 36); the absence of optical exaltation in this hydrocarbon is wholly unexpected; but, on the other hand, the type of compound is entirely new. With benzene also the distribution of valency within the molecule differs from that in any known compound; our knowledge of it, admittedly far from complete, has been gained from the chemical side, and is summarised in the various structural formulæ; but the limitations of the physical method of attack can be traced from Thomsen's endeavour to determine its structure from thermochemical data (Note 37) to the more recent invention of isorropesis. And, despite the evidence obtained from refractivities, we may not unreasonably demur to the suggestion that derivatives of benzene, which by their behaviour towards substituting agents show themselves to be wide apart in chemical properties, such as nitrobenzene and aniline on the one hand or chlorobenzene and phenol on the other, should respectively be classified together (Note 38). Undoubtedly, most useful information is obtained from a comparison of the physical properties of two related substances, the exact constitution of one of which is uncertain, but that of the other known. Therefore, bearing in mind the great development that has taken place recently in the correlation of physical properties with chemical constitution by methods based on refraction and absorption, every chemist will welcome the entry of Dr. Lowry into that field of research on the relation between magnetic rotation and structure, which for all time will be associated with Sir William Perkin's name.

Substitution in the Benzene Series.

Turning now to a discussion of the problem of substitution in cyclic compounds, one important factor must not be overlooked; the even distribution of the residual affinity of the benzene molecule is disturbed by the introduction of a substituent. The study of substitution in benzene derivatives indicates that, as a consequence of this disturbance, a directing influence comes into play which, when the substituent is changed, may vary in the effect it exercises on the course of substitution.

Arising probably from this even distribution of valency it is characteristic of benzene to furnish additive compounds in which six atoms of hydrogen or a halogen, but not two or four, become attached symmetrically to the molecule; substitution, however, occurs when a catalyser is present, such as the aluminium mercury couple for halogenation, or sulphuric acid for nitration or sulphonation, leading initially to the production of mono-substituted derivatives. Whether the catalyser by association with the benzene molecule (Note 39) limits this additive capacity, or whether its function is to promote the elimination of the halogen acid or water respectively (Note 40), is still a subject of discussion, but in the absence of a reaction of additive type it is not easy to account for facts such as the production of a certain amount of trinitrophenol when benzene is nitrated in the absence of sulphuric acid.



(Note 41)

The much-debated questions still remain: Why and by what mechanism, when a second or third substituent is introduced into the molecule, is the orientation of the isomeric products determined by the radical or radicals already present? For disubstitution, the *ortho-para-* and the *meta-*laws have been deduced, and the radicals which respectively promote mainly *ortho-para* substitution on the one hand and *meta-*substitution on the other have been catalogued (Note 42). But these laws take account only of the orientation of the chief product or products, whereas all three derivatives, *ortho*, *meta*, and *para*, have been detected in most of the reactions studied, and their relative proportion in many cases is known to depend on the conditions, being affected by such influence as variations in temperature or in the medium employed (Note 43). Nitration of acetanilide, for example, furnishes a mixture of *ortho-* and *para-*nitracetanilide, but of aniline in the presence of much sulphuric acid yields chiefly *meta-*nitraniline (Note 43). And, to illustrate the inadequacy of the *meta* law, the fact that sulphonation of benzenesulphonic acid with concentrated sulphuric acid at 230—240° furnishes an equilibrium mixture of the *meta-* and *para-*disulphonic acids in the proportion of 2 : 1 may be quoted (Note 44).

In the exploration of this field many workers have participated, but the results, recorded almost as often in patent specifications as in journals, are seldom quantitative, so great is the difficulty at times in isolating the minor product or products of the change. Recently, however, by a most ingenious use of melting-point curves and density determinations, Holleman and his colloborators have carried out an exhaustive series of substitutions with small quantities of material and under known conditions (Note 45); yet after a survey of the whole field the conclusions reached are:—

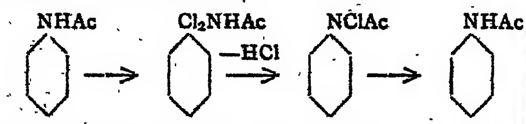
1. That uncertainty cannot be removed until some basis exists for different reactions to be carried out under comparable conditions (Note 46).

2. That even if the relative amounts of the isomerides formed when a radical C is introduced into each of the mono-substitution derivatives C_6H_5·A and C_6H_5·B be known, it is not possible to calculate the proportion in which the isomerides C_6H_3·ABC will be produced when the radical C is substituted in the compound C_6H_4·AB.

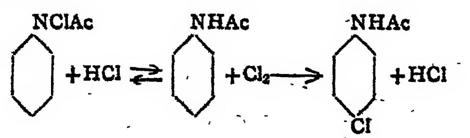
Although the validity of the *ortho-para-* and of the *meta-*laws may be impeached, they serve as a first approximation, and many theories have been propounded to account for them. Armstrong has suggested that in *ortho-para-*substitution the additive compound is formed by association of the addendum with the carbon atom carrying the radical already substituted in the molecule (Note 47), whereas in *meta-*substitution it arises by union of the addendum with this radical (Note 48), transformation to the respective disubstitution derivatives being effected

possibly in step-by-step progression, as conjectured by Lapworth (Note 49). Holleman, who also adopts the additive hypothesis, is of the opinion that the radical already present in the molecule may promote or retard the association of the addendum with the pair of carbon-atoms, to one of which it is itself attached. By the operation of the first of the alternatives an *ortho-* and by conjugation a *para*-derivative will arise; from the second a *meta*-derivative will result, when scission of the additive compound ensues. Holleman's is the only hypothesis which has been submitted to the test of quantitative investigation, and although, as already mentioned, the results do not suggest that finality has been reached, it marks an advance in the study of this obscure problem (Note 50).

No discussion of substitution in the benzene series would be adequate without reference to the remarkable behaviour of amines and phenols. Unlike other mono-substitution derivatives, which do not differ markedly from benzene in reactivity, these furnish mono-, di-, and tri-derivatives very readily. With aniline or acetanilide, substitution occurs first of all in the side-chain, being followed under appropriate conditions by removal of the substituent from the amino-group and entry into positions relatively *ortho-*, *para*, or both *ortho-* and *para* to it. The earliest of these changes to be studied was the transformation of methylaniline into *para*-toluidines; many of them have been discovered by Chattaway and his collaborators, and until a critical study of the chlorination of acetanilide was undertaken by Orton and Jones (Note 51), it was held that the changes, which occur only in the presence of hydrochloric acid, were of the type:—

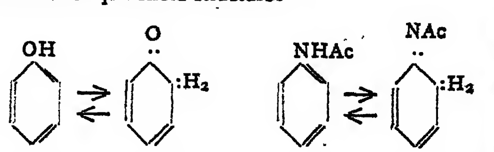


From the dynamics of the reaction, it is now known that intra-molecular transformation from the side-chain to the ring does not occur, the agent promoting the substitution being chlorine arising from the following series of reactions:—



As bromination has been shown to follow the same course, it is evident that no secure foundation now exists for the view, formerly widely held, that the reactivity of amines is intimately connected with the variable valency of nitrogen leading to initial substitution in the side-chain.

Even were this view, now discredited, still applicable to the amines, it could not be extended with the same certainty to the phenols. Hence, in explanation of the rigid adherence to the *ortho para-* law observed among the mono-substitution derivatives of these two groups of compounds, it is noteworthy that Thiele (Note 52), for the phenols, suggests that the reactivity may be due to these substances being stable enolic forms of ketodihydrobenzenes, and that Orton (Note 53), for the amines, conjectures that it may arise from the formation of dynamic isomerides of quinonoid structure:—



How far these suggestions may open up a new field of inquiry into the "mechanism" of substitution remains to be seen; it is at least interesting that their extension to the naphthalene series shows that not only does the reactivity of the naphthols and of α-naphthylamine recall that of phenol and aniline, but the orientation of their mono-substitution derivatives (Note 54) in almost every case is the same as that of one or other of the six naphthaquinones, the existence of which has been predicted by Willstätter (Note 55).

Notes.

1. These schools in 1881 became the Normal School of Science, and in 1900 the Royal College of Science, now incorporated in the Imperial College of Science and Technology.

2. J. N. Collie and H. S. Patterson, *Trans. Chem Soc.*, 1913, ciii., 419; *Proc. Chem. Soc.*, 1913, xxix., 217.

3. Sir J. J. Thomson, *Proc. Roy. Soc.*, 1913, lxxxix., A, 20.

4. A. Claus, *Ber.*, 1881, xiv., 435. It may be noted that Claus concludes his paper with the statement, " . . . die Annahme von Valenzen als in den mehrwerthigen Atomen präexistirender ihrer Wirkungsgrösse nach bestimmter Anziehungseinheiten eine ebenso unbegründete, wie unnatürliche Hypothese ist."

5. A. Werner, " Neuere Anschauungen auf dem Gebiete der anorganischen Chemie" (Friedr. Vieweg u. Sohn, Braunschweig, 1908); English edition, "New Ideas on Inorganic Chemistry," E. P. Hedley. (Longmans, 1911).

6. A. Werner, *Ber.*, 1911, xliv., 2445, 3231.

7. S. U. Pickering, *Proc. Chem. Soc.*, 1885, i., 122; H. E. Armstrong, *Proc. Roy. Soc.*, 1886, xl., 285.

8. As an example of the unsatisfactory character of the doubly linked formula to which the older meaning was attached, the following may be quoted:—*unsym.*-Diphenyldichloroethylene, like ethylene, combines molecularly with bromine, but tetraphenylethylene does not.—

$$\begin{array}{c}CH_2\\ \|\\ CH_2\end{array} \qquad \begin{array}{c}C(C_6H_5)_2\\ \|\\ C\,Cl_2\end{array} \qquad \begin{array}{c}C(C_6H_5)_2\\ \|\\ C(C_6H_5)_2\end{array}$$

yet a similar structure has been assigned to each (Biltz, *Annalen*, 1897, ccxcvi., 219).

9. P. F. Frankland, *Proc. Chem. Soc.*, 1913, xxix., 101.

10. J. Volhard, *Annalen*, 1887, ccxlii., 141; *Ber.*, 1888, xxi., 1904.

11. L. Van Raymenant, *Bull. Acad. Roy. Belg.*, 1900, p. 724. For the chloroketobutanes, *cf. Idem.*; Kling, *Comptes Rendus*, 1905, cxl., 312; *Bull. Soc. Chim.*, 1905, [3], xxxiii., 322.

12. A. Michael, *Ber.*, 1901, xxxiv., 4035, 4046.

13. C. Montemartini, *Gazz. Chim. ital.*, 1897, xxvii., [2], 368; 1898, xxviii., [2], 290).

14. It may be of interest to note that the long controversy respecting the composition of ordinary ethyl acetoacetate, $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}OEt$, the first of these desmotropic compounds to be discovered, has been brought to an end by the isolation of each desmotropic form at temperatures sufficiently low to inhibit the desmotropic change. From refractometric observations with mixtures of the pure isomerides, Knorr concludes that this ester at the ordinary temperature contains about 2 per cent of the enolic form, whereas from bromination experiments with the etser itself, which may possibly be accompanied by a disturbance of the equilibrium, K. H. Meyer infers that the amount may be as much as 7 per cent. (L. Knorr, O. Rothe, and H. Averbeck, *Ber.*, 1911, xliv., 1138; K. H. Meyer, *Annalen*, 1911, ccclxxx., 222; K. H. Meyer and P. Kappelmeier, *Ber.*, 1911, xliv., 2718).

15. A. Lapworth, *Trans. Chem. Soc.*, 1904, lxxxv., 31; H. M. Dawson with May S. Leslie, *Ibid.*, 1909, xcv., 1860; with R. Wheatley, *Ibid.*, 1910, xcvii., 2048: with F. Powis, *Ibid.*, 1912, ci., 1503.

16. K. H. Meyer, *Ber.*, 1912, xlv., 2867.

17. O. Aschan, *Ber.*, 1912, xlv., 1913; 1913, xlvi., 2162; K. H. Meyer, *Ber.*, 1912, xlv., 2868.

18. J. Volhard, *loc. cit.*

19. O. Schütz and W. Marckwald, *Ber.*, 1896, xxix., 58.
20. H. Leuchs, *Ber.*, 1913, xlvi., 2435.
21. S. Arrhenius, "Theories of Chemistry," edited by T. Slater Price (Longmans, 1907), p. 76.
22. J. U. Nef, "The Fundamental Conceptions underlying the Chemistry of the Carbon Atom," *Journ. Am. Chem. Soc.*, 1904, xxvi., 1566.
23. A. Michael, *Ber.*, 1901, xxxiv., 4028, covering reference to earlier papers.
24. B. Flürscheim, *Trans. Chem. Soc.*, 1909, xcv., 721.
25. P. Walden, *Ber.*, 1895, xxviii., 1297; W. A. Tilden and B. M. C. Marshall, *Trans. Chem. Soc.*, 1895, lxvii., 494.
26. E. Fischer, *Annalen*, 1911, ccclxxxi., 123.
27. A. Werner, *Ber.*, 1911, xliv., 873.
28. P. Pfeiffer, *Annalen*, 1911, ccclxxxiii., 123.
29. P. Walden, *Ber.*, 1896, xxix., 133; 1897, xxx., 3146; 1899, xxxii., 1833, 1855.
30. Without the aid of a model it is not possible to show that the production of the *dextro-* or *lævo*-acid may be accounted for by the hypothesis that an intermediate additive compound is formed, which undergoes scission in one or other of two ways. Diagrams of models will be found in Fischer's paper (*loc. cit.*, *cf.*, *Annual Reports on the Progress of Chemistry* (Gurney and Jackson), 1911, viii., 67), and to illustrate Werner's hypothesis, which is more explicit than Fischer's, in a paper by W. E. Garner (*Proc. Chem. Soc.*, 1913, xxix., 200).
31. P. F. Frankland, "The Walden Inversion," Presidential Address to the Chemical Society (*Trans. Chem. Soc.*, 1913, ciii., 713).
32. J. Theile, *Annalen*, 1899, cccvi., 126.
33. H. E. Armstrong, *Trans. Chem. Soc.*, 1897, li., 264 (footnote).
34. R. Willstätter and E. Wasser, *Ber.*, 1911, xliv., 3423.
35. *Cf.*, J. W. Brühl, *Ber.*, 1907, xl., 878; Sir W. H. Perkin, *Trans. Chem. Soc.*, 1907, xci., 806, for references to earlier papers.
36. A. Hantzsch, *Ber.*, 1912, xlv., 563; K. Auwers, *Ibid.*, 971.
37. *Cf.*, H. E. Armstrong, *Phil. Mag.*, 1887, [5], xxiii., 73; J. W. Brühl, *Journ. Prakt. Chem.*, 1887, [2], xxxv., 181, 209.
38. *Cf.*, J. W. Brühl, *Zeit. Phys. Chem.*, 1894, xvi., 220; Smiles, "Relations between Chemical Constitution and Physical Properties" (Longmans, 1910), p. 299.
39. B. N. Menschutkin, Abstr. *Chem. Soc.*, 1912, cii., [1], 98—100.
40. *Cf.* H. E. Armstrong, *Trans. Chem. Soc.*, 1887, li., 263.
41. The phenyl by nitration forming the trinitro derivative (picric acid), Armstrong and Rossiter, also Groves, *Proc. Chem. Soc.*, 1891, vii., 89.
42. *Cf.* Noelting, *Ber.*, 1876, ix., 1797; Armstrong, *Trans. Chem. Soc.*, 1887, li., 258; Crum Brown and Gibson, *Ibid.*, 1892, lxi., 367.
43. Hübner, *Annalen*, 1881, ccviii., 299.
44. J. J. Polak, *Rec. Trav. Chim.*, 1910, [ii.], xiv., 416; R. Behrend and M. Mertelsmann, *Annalen*, 1911, ccclxxviii., 352.
45. A. F. Holleman, "Die Direkte Einführung von Substituenten in den Benzolkern" (Leipzig, Viet and Co., 1910), p. 215.
46. For example, nitration is effected chiefly at low temperatures, but sulphonation of mono-substituted benzenes at temperatures higher than the ordinary, which if employed in nitration would lead to mixed products.
47. Kinetic studies of the chlorination and bromination of toluene, $C_6H_5 \cdot CH_3$, however, gave no indication of the production of an intermediate additive compound of the hydrocarbon and addendum (*cf.* Holleman, Polak, van der Laan, and Euwes, *Rec. Trav. Chim.*, 1908, xxvii., 435; Brunner and Dluska, *Bull. Acad. Sci.*, Cracow, 1907, p. 693; Bancroft, *Journ. Phys. Chem.*, 1908, xii., 417; Cohen, Dawson, Blockey, and Woodmansey, *Trans. Chem. Soc.*, 1910, xcvii., 1623).
48. H. E. Armstrong, *Trans. Chem. Soc.*, 1887, li., 258.
49. A. Lapworth, *Trans. Chem. Soc.*, 1898, lxxiii., 454; 1901, lxxix., 1265.
50. It should be mentioned that other views, based on the loosening or strengthening of the affinity of the hydrogen atoms situated in *ortho-*, *para-*, or in *meta-* positions, brought about by the disturbing influence of the radical already present in the molecule on the valency of the carbon atom to which it is attached, and therefore on that of the other five carbon atoms, have been advanced by Flürscheim (*Journ. Prakt. Chem.*, 1902, [ii.], lxvi., 321), Tschitschibabin (*Ibid.*, 1912, [ii.], lxxxvi., 397), and others.
51. K. J. P. Orton and W. J. Jones, *Brit. Assoc. Report*, 1910, p. 96; *Trans. Chem. Soc.*, 1909, xcv., 1456.
52. J. Thiele, *Annalen*, 1899, cccvi., 129.
53. British Association Report, 1910, p. 96.
54. *Cf.*, W. P. Wynne, art. "Naphthalene," Thorpe's *Dictionary of Applied Chemistry*, second edition, vol. iii. (Longmans, 1912).
55. R. Willstätter and J. Parnas, *Ber.*, 1907, xl., 1406.

(To be continued).

THE SCIENTIFIC WEEK.

(From Our Own Paris Correspondent).

PARACHUTES FOR AEROPLANES.

The audacious experiment of the aviator Pégond, who at a height of 300 metres left his aeroplane to descend to the ground by the help of a parachute, has brought to the front the interesting question of parachutes for aeroplanes. It was only about the year 1910 that the idea of employing parachutes for assuring the safety of aviators was considered for the first time. Until then security was sought for only in the qualities inherent to the machine, any additional apparatus being considered inefficacious, if not dangerous. The problem of the use of parachutes is, indeed, a very particular one, for these apparatus must be ready to act whatever may be the position, speed, and height of the avion to which they are attached. That is the real difficulty of the problem, a difficulty that a large number of inventors seem to ignore systematically. Ordinary experiments, in which the parachute is, at the start, placed in a convenient position, animated by a very slow speed, sometimes even with no speed at all, being far removed from the real conditions in which the apparatus has to work in all positions and at speeds of more then 100 kilometres an hour, and especially instantaneously in order that its efficacy may be immediate. Lastly, it must be remembered that to descend a weight of 75 kilogrms. at a speed of 4 or 5 metres per second the surface of the parachute must have a development of 60 square metres. It is, then, the complete condemnation of parachute garments, of which the most sadly celebrated were those of Reicheld, which caused the death of their inventor during an experiment at the Eiffel Tower. That is also the reason of the repeated failures of parachutes of the umbrella system with stiff frames, the development of which is very uncertain. The only apparatus that, up till now, have given good results are the supple parachutes, of which the principal ones are those of Hervieux, Cremoux, Dangy-Baillet, Bonnet, and Ochs. What characterises them all is the special arrangement enabling their instantaneous development, which is, indeed, the essential condition required. In the Hervieux parachute, the prototype of the kind, the buffer springs are placed all along the periphery of the parachute, which is enclosed in a case, and the springs are then strongly compressed. When a little spring is pressed the box opens, and the springs of the parachute shoot out violently, thus determining the immediate development of the silk of the parachute. In the Dangy-Baillet, Crémoux,

and Bonnet parachutes it is a buffer filled with air, running along the whole or part of the periphery that produces the opening of the machine. In the Ochs system it is steel springs that do the work.

THE STRUGGLE AGAINST TUBERCULOSIS.

Recently at the Academy of Sciences, M. Chauveau spoke of one of the means advised for fighting against tuberculosis—obligatory declaration. The advantages to be drawn from this declaration are perhaps somewhat illusory. Of what use will it be? Of none; for it is impossible to fight against the propagation of the germs. And then, again, says he, the germ is nothing after all; it is the ground that is everything. We live in an environment infected with myriads of tuberculous germs and yet we are not all tuberculous. Only weakened organisms are affected, healthy organisms are refractory. M. Chauveau next calls attention to a long and costly experiment that he made concerning the virulence of tuberculosis, on a lot of 60 oxen that he had to feed for a long period before having them successively slaughtered. He likewise recalls an experiment of clavelous contamination of which he is the author.

STUDY OF ROLLING OF SHIPS.

M. Bertin, Chief Engineer for Naval Ship Building, when presenting, before the Academy of Sciences a work of M. Bogaert, a Belgian engineer, on the gyroscopic effect, especially brought to notice the study made in this work of the old pegged oscillograph, which was the first instrument employed to measure rolling. On this occasion he retraces the history of the double oscillograph which he employed for his observation on swell and rolling. The first instrument, a simple trial model, dates from 1868; it was supplied with two pendulums, one of long, the other of short period. The first pendulum could not reach the duration required, and that led M. Bertin to propose the combination of the gyroscope and the short pendulum which has never yet been realised. In 1871, in England, Mr. William Froude constructed an oscillograph with two pendulums, one of which was a large pendulum of a suitable period. From this example, the following year M. Bertin had an apparatus constructed conformable to his first idea, and which has given good results.

THE INDIVIDUALITY OF PROTOZOA.

The question has often been discussed to know if the protozoa, which frequently divide into two, keep or lose their individuality after this division. If, indeed, they kept it they would be immortal, since they can keep on dividing themselves indefinitely when they are in a suitable environment. Weissman had also affirmed their immortality, that he opposed to the precarious duration of the bodies of higher animals. But this immortality does not appear to exist according to the latest experiments of Metchnikoff, who fed Paramesies with carmine grains. They at first swallow a great quantity, but after a few days they learnt to refuse them, and no longer swallow a single grain. Now if at this moment the Paramesie divides the individual daughters have lost all remembrance of the former experiments and again absorb the carmine. The protozoa that divides itself seems to cease to live as an individual and to give birth to two individuals, completely new; it is, then, not immortal.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Academie des Sciences. Vol. clvi., No. 26, June 30, 1913.

Preparation of Diphenylpentanes and the Corresponding Dicyclohexylpentanes.—Paul Sabatier and M. Murat.—By direct hydrogenation over nickel of the corresponding acids the authors have prepared three of the eighteen possible diphenyl hydrocarbons derived from pentane or its isomers, viz., 1·5-diphenyl pentane from normal pentane and two from methyl-2-butane. When subjected to direct hydrogenation over nickel they are all converted into the corresponding dicyclohexylic hydrocarbons. It is noticeable that all the diphenyl hydrocarbons are fluorescent, especially those of normal structure which possess a formic chain with a phenyl group at each end. The dicyclohexylic compounds are not fluorescent.

Hydrates of Uranic Anhydride and Heat of Formation of Uranyl Nitrate.—M. de Forcrand.—Uranic acid, $UO_3.H_2O$, is a fairly stable hydrate which boils at about 220° C. The dihydrate boils at 135° and effloresces rapidly at 80°. It loses a molecule of water (slowly) over sulphuric acid. The heat of formation of $N_2O_6UO_2$(solid) from UO_2 (sol.) O_6 (gas) and N_2 (gas), is +67·25 cal., and of $N_2O_6UO_2$ (dissolved) +86·25 cal. These values approach those given by copper.

Chemical Lability and Absorption of Ultra-violet Rays.—Victor Henri.—According to the electronic theory of chemical reactions a substance which reacts easily contains molecules which can easily liberate or exchange electrons, and the bonds between the atoms in the molecules are produced by electrons. The absorption of ultra-violet rays being an electronic property it might be supposed that there is a connection between the absorption and the lability of substances. This conjecture is confirmed by the study of series of substances belonging to the same chemical families, some being stable and the similar ones labile. It is observed that substances the molecules of which are labile strongly absorb the ultra-violet rays.

Action of CO_2 on Mineral Sulphides. — N. D. Costeanu.—CO_2 has no action on the sulphides of silver, copper, cadmium, bismuth, and antimony when they are heated in an electrical resistance furnace and exposed to its action. With sulphide of silicon it gives silica, carbon monoxide, and sulphur, $2CO_2+SiS_2=2CO+2S+SiO_2$.

Composition of Gaseous Mixtures resulting from the Action of Water on Carbides of Uranium and Thorium.—P. Lebeau and A. Damiens.—When water acts on uranium carbide the gaseous mixture evolved has approximately the same composition when the same specimen is tested twice, but carbides containing graphite give very different results from those which contain no graphite. The former gave roughly 50 per cent of hydrogen, 24 per cent of ethane, and 13 per cent of methane, while the gases from non-graphitic specimens contain less free hydrogen and more methane, propane, butane, &c.

Azoic Colouring Matters from Phenylisoxazolone.—André Meyer.—The author has prepared various dyes, both acid and substantive, from phenylisoxazolone, *e.g.*, benzene *p*-sulphonate of sodium-azophenylisoxazolone, in order to compare their tinctorial properties with those of the pyrazol dyes. The colours they produce are very often very similar to those produced by the corresponding derivative of pyrazol, but they exhibit much less resistance to the action of light.

Composition of Water Gas.—Leo Vignon.—Water gas consists essentially of nearly equal volumes of carbon monoxide and hydrogen. It also contains carbon dioxide, and the author has proved that a small proportion of methane is always present. It is formed by the following reactions:—

$$4CO+2H_2O = 3CO_2+CH_4$$
$$2CO+2H_2 = CO_2+CH_4$$
$$CO_2+4H_2 = CH_4+2H_2O.$$

Existence of Bromites.—J. Clarens.—When a solution of hypobromite is raised to about 80° and then treated with an excess of ammoniacal salt it contains a compound which reacts in the cold on arsenious acid but has no action on ammoniacal salt. It is thus neither bromate nor hypobromite, but is probably bromite of formula BrO_2M.

THE CHEMICAL NEWS.

VOL. CVIII., No. 2809.

ADDRESS TO THE CHEMICAL SECTION OF THE BRITISH ASSOCIATION.

BIRMINGHAM, 1913.

By Prof. W. P. WYNNE, D.Sc., F.R.S., President of the Section.

(Concluded from p. 149).

Symmetric and Asymmetric Syntheses.

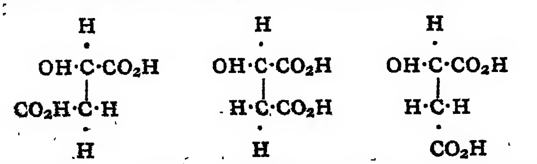
IT must not be supposed that the "mechanism" of substitution can be explained by reference only to the examples of this type of reaction which have been mentioned, or that the summary attempted in the restricted field of the replacement of hydrogen by halogen is a complete picture of all the different views advanced to account for this chemical change. Rather, the effort has been made to indicate in broad outline the difficulties that beset any exploration of that debateable region which lies between the two sides of a chemical equation. But, as the wonderful story of carbon chemistry shows, the failure to comprehend the processes operative in substitution does not impede rapid progress in other directions. The study of the mobility of radicals, desmotropy being only one of many examples of this phenomenon, continues to present fresh problems, of which that raised by Thorpe (Note 56) in connection with the mobile hydrogen atom of glutaconic and aconitic acids may be mentioned, as it revives a question of old standing: Do free units of valency exist in carbon compounds? The syntheses of caffeine and certain alkaloids, of sugars and peptone-like polypeptides, of natural terpenes and camphor, of indigo and rubber, are well-known achievements, while natural processes, in which enzyme action plays a part, are yielding their closely guarded secrets to the persistent inquiry of Armstrong and his collaborators, who are probing the relationship between enzyme and substrate which Emil Fischer pictured as that of lock and key. Further, there is that large field of work which includes not only the Walden inversion but new problems of asymmetry, with which the names of Frankland, Pope, Werner, and others are associated; while Barlow and Pope's conception of the relation of valency to atomic volume, by correlating crystalline structure with the composition, constitution, and configuration of carbon compounds, has given a new interest so the study of crystallography.

Nor is progress less rapid in that other important branch of chemistry—the unravelling of the structure of natural products. The constitution of rubber is approximately known; most of the alkaloids have been explored with a greater or less degree of completeness; and now the study of starch (Note 57), chlorophyll, and hæmatin (the non-proteid constituent of hæmoglobin) (Note 58) has been taken up afresh during the last three years, with results which, in the case of the two latter, eclipse in importance and interest all that was previously known. In whatever direction we may look, there is the same evidence that we can take to pieces the most complicated structure which nature has devised, and by the aid of valency conceptions can fit the pieces into a formula which is an epitome of the chemical activities of the molecule. Again, in many cases the resources of our laboratories enable us to build up the structure thus displayed, and to establish the identity of nature's product and our own. Nevertheless, the fact remains that all these syntheses leave untouched and unexplained the profound difference between the conditions we find necessary to achieve our purpose and those by which the plant or animal carries on its work in presence of water and at a temperature differing only slightly from the normal. It is, of course, a well-known fact that an enzyme under the appropriate conditions can bring about the same chemical transformation of a substrate as is effected by the living cell from which it can be separated; but our knowledge of these complex, ill-defined, nitrogenous organic compounds is relatively very meagre; they are difficult to purify, and their composition—apart from any question of structure—is largely unknown. Yet because Wöhler chanced to discover that urea can be produced synthetically from an inorganic source the conclusion is not infrequently drawn that all chemical changes in living substance are brought about by ordinary chemical forces (Note 59). Probably everyone present will concur in that view, but the assent, if given, can hardly arise from a consideration of the facts, of which there is no great store. Where so little is known accurately, chemistry is not on very safe ground if she infer the rest. What common basis of comparison exists between Wöhler's process and the metabolic changes by which urea is produced in the living body? What evidence have we that because an enzyme and an inorganic agent under different conditions give rise to the same end product, the driving force is the same, although the lines along which it is exercised are very different? I think it is not the least of the many services which Prof. Meldola has rendered to chemistry, that he has given us this warning:—"If we have gone so far beyond Nature as to make it appear unimportant whether an organic compound is producible by vital chemistry or not, we are running the risk of blockading whole regions of undiscovered modes of chemical action by falling into the belief that known laboratory methods are the equivalents of unknown vital methods" (Note 60).

I turn now to a no less interesting question than that involved in enzyme reactions, namely, the wide distribution in plants and animals of single asymmetric substances which if synthesised in the laboratory would be produced as inactive mixtures of both asymmetric forms. It has been argued that the occurrence of racemic compounds in nature, although infrequent, is a proof that in the organism, as *in vitro*, they are in all cases the initial products from which, when separated into antipodes, one of the asymmetric compounds is utilised in the life processes and the other left. But whether this be the case, or whether only the one asymmetric form result from the synthesis, Pasteur fimly held the view that the production of single asymmetric compounds or their isolation from the inactive mixture of the two forms is the prerogative of life. Three methods were devised by Pasteur to effect this isolation, and in only one of them are living organisms—yeasts or moulds—employed; but Prof. Japp, in his address to this Section at Bristol in 1898, emphasised the fact, hitherto overlooked, that in the two others, nevertheless, "a guiding power [is exercised by the operator] which is akin in its results to that of the living organism, and is entirely beyond the reach of the symmetric forces of inorganic nature." Hence, to quote again from his address, "only the living organism with its asymmetric tissues, or the asymmetric products of the living organism, or the living intelligence with its conception of asymmetry, can [bring about the isolation of the single asymmetric compound]. Only asymmetry can beget asymmetry." After an exhaustive review of the subject, Japp came to the conclusion that the failure to synthesise single asymmetric compounds without the intervention, either direct or indirect, of life is due to a permanent disability, and although—as was to be expected—this conclusion was challenged (Note 61), the only "asymmetric syntheses" effected since that time have been operations controlled by the chemical association of an optically active substance with the compound undergoing the synthetical change (Note 62).

Recently the problem has assumed a more hopeful character. Ostromisslensky (Note 63) in 1908 made the remarkable discovery that inactive asparagine, which is not racemic but a mixture of the *dextro-* and *lævo-*forms in molecular proportion, gave a separation of one or othe

isomeride when its saturated solution was inoculated by a crystal of glycine—a substance devoid of asymmetry. Now Erlenmeyer claims to have achieved a true asymmetric synthesis by boiling an aqueous solution of inactive asparagine for sixteen hours, when by crystallisation part of the *dextro*-form separated in an almost pure state (Note 64). The theoretical conclusions which led to this investigation are of much interest because they raise afresh the question whether without displacement of the individual radicals, and apart from antipodes, more than one compound can exist, in the molecule of which two carbon atoms are united by a single linking (Note 65). As an illustration, reference may be made to the malic acid series, in which three optically active compounds are known, the *dextro*-acid, the *lævo*-acid, and Aberson's acid (Note 66). In the *lævo*-series the three isomerides obtainable by rotation of one of the carbon atoms with its attached radicals relatively to the other would be—



Lævo-acid, $[\alpha]_D$ $-5 \cdot 8°$. (Not isolated). Aberson's acid, $[\alpha]_D$ +9 8°.

With the inactive asparagine it is supposed by Erlenmeyer that prolonged heating in aqueous solution produces a rotation of this type, possibly to an unequal extent or in opposite directions in the *dextro*- and *lævo*-forms, whereby the products being no longer antipodes become separable by ordinary laboratory methods. It is too early yet to say whether, by exclusion of all asymmetric influences, the riddle has been solved, but it is easy to understand with what interest confirmation of Erlenmeyer's results is awaited.

Honours Students and Post-Graduate Scholarships.

In bringing this address to a conclusion, it will not be an innovation if I refer—it shall be only briefly—to the training of those who will carry on and amplify the work which we in this generation have attempted to do. This section stands for the advancement of chemistry which includes, so closely are pure and applied chemistry intertwined, the advancement of chemistry as applied to industry. Once again the cry has been raised in the press (Note 67) that chemists trained in our Universities are of little value in industrial pursuits; they are too academic; they are not worth their wage—little as that often is, whether judged by a labourer's hire or the cost of a university training. It may be so. On the other hand, it is possible the employer obtains all that he pays for, and by paying more would receive in return much more by the inducement offered to more highly trained men to enter the field. Three years' training for the ordinary degree cannot carry a student very far in chemistry, and this preliminary training—for it is little more—is insufficient to equip the young graduate for more than routine work. With the Honours student it is otherwise. He must either enter on his three years' residence at a University with a knowledge which does not fall below the requirements of the Intermediate Examination, and devote the greater part of his time to his Honours subject, or he must be prepared to spend a fourth year to reach the necessary standard. More highly equipped in the academic sense than a man who has worked only for the ordinary degree, he undoubtedly is, yet there is seldom time to begin his training in research methods or in methods of commercial analysis where rapidity rather than extreme accuracy is the object in view.

Two reforms, I venture to think, are needed: the first would avoid early specialisation, which is apt to be disastrous, the second would encourage post-graduate training in directions where the student's inclinations or aptitude may be stimulated and developed. If the Civic Universities, established in virtue of charters drafted mainly on similar lines and inspired by similar aims, could come to some agreement requiring three years' residence, subsequent to the Intermediate, for an Honours degree in chemistry, the first reform would be effected—it is a measure for which a strong case can be made out. If, further, they could see their way to standardise their Ordinances and Regulations for the M.Sc. degree, cease to confer it on Honours graduates of one or more years' seniority in return for payment of a fee, and confine it to graduates - not necessarily Honours graduates—who have carried out an approved piece of research during not less than one academic year, Selection Committees, Boards of Directors, or individual employers would have some clue to the type of man before them. I would go further and suggest that the interchange of Honours graduates between the Civic Universities, or between them and other Universities or Colleges, if it could be arranged, would be of much benefit to the student himself. No University in this country is wealthy enough to attract to its service teachers who are pre-eminent in each branch of chemistry. How great, then, would be the gain to an Honours graduate working for the M.Sc. degree, if, instead of being associated with the same teacher during the whole of his academic career, he could migrate from the place which had trained him to spend part, or the whole, of his time in the laboratory of an Armstrong, a Donnan, a Perkin, or a Ramsay, during that most critical period when he is sorting out his own ideas and learning how to use his fingers and his wits. But whether enforcement of the longer training for the Honours degree be possible; whether a research degree as a step to the Doctorate be desirable or practicable, there can be no doubt that the urgent need of the present time is the provision of scholarships and exhibitions, sufficient in value to secure at least a bare livelihood, for post-graduate work. He who is able to convert Education Committees and private donors to the view that a far better return for the money could be assured if part of the large expenditure on scholarships for matriculated or non-matriculated students were diverted to post-graduate purposes, will have done a service to science and the State the value of which, in my opinion, cannot be overestimated.

Notes.

56. N. Bland and J. F. Thorpe, *Trans. Chem. Soc.*, 1912, ci., 871, 1490.

57. H. Pringsheim and H. Langshans, *Ber.*, 1912, xlv., 2533.

58. For summaries of Willstätter's and Marchlewski's "Researches on Chlorophyll," and of Piloty's on "Hæmatin," *cf. Annual Reports on the Progress of Chemistry* (Gurney and Jackson)), 1911, viii., 144—152; 1212, ix., 165—172.

59. "Quite similar changes can be produced outside the body (*in vitro*) hy the employment of methods of a purely physical and chemical nature. It is true that we are not yet familiar with all the intermediate stages of transformation of the materials which are taken in by the living body into the materials which are given out from it. But since the initial processes and the final results are the same as they would be on the assumption that the changes are brought about in conformity with the known laws of chemistry and physics, we may fairly conclude that all changes in living substance are brought about by ordinary chemical and physical forces."—Sir Edward Schäfer, President's Address at the Dundee Meeting, British Association Report, 1912, p. 9.

60. R. Meldola, "The Chemical Synthesis of Vital Products" (Arnold, 1904), p. 7.

61. F. R. Japp, "Stereochemistry and Vitalism." Presidential Address to Section B (Bristol), British Association Report, 1898, p. 826; *cf.* K. Pearson, *Nature*, 1898, lviii., 495; G. Errara; F. R. Japp, *Ibid.*, p. 616;

Ulpiani and Condelli, *Gazz. Chim. ital.*, 1900, xxx., [i.], 344; Byk, *Ber.*, 1904, xxxvii., 4696; Henle and Haakh, *Ber.*, 1908, xli., 4261; Byk, *Ber.*, 1909, xlii., 141.
62. *Cf.*, *inter alia*, McKenzie, *Trans. Chem. Soc.*, 1905, lxxxvii., 1373.
63. I. von Ostromisslensky, *Ber.*, 1908, xli., 3035.
64. E. Erlenmeyer, *Biochem. Zeit.*, 1913, lii., 439.
65. *Cf.* J. Wislicenus, *Ueber di räumliche Anordnung der Atome in organischen Molekulen* (Leipzig, Hirkel, 1889), 28; K. Auwers and V. Meyer, *Ber.*, 1888, xxi., 791.
66. J. H. Aberson, *Ber.*, 1898, xxxi., 1432; P. Walden, *Ber.*, 1899, xxxii., 2720.
67. *Cf. The Times*, Engineering Suppl., 1913, May 7, 21, 28, June 4, 11, 18.

THE PROGRESSIVE BROMINATION OF TOLUENE.*

By JULIUS B. COHEN and P. K. DUTT.

A. K. Miller (*Trans.*, 1892, lxi., 1023) studied the action of bromine on ortho- and para-bromotoluene separately and identified the dibromotoluenes formed in each case by oxidising the products to the corresponding benzoic acids and fractionally crystallising the barium salts. His results may be summarised as follows:—Ortho-bromotoluene gave the 2:5-dibromo- compound as the principal product together with a smaller quantity of the 2:4-derivative; para-bromotoluene gave, as the main product, 3:4-derivative and a smaller quantity of the 2:4 compound.

In comparing these results with those of chlorination of ortho- and para-chlorotoluenes (Cohen and Dakin, *Trans.*, 1901, lxxix., 1111) considerable discrepancies appear. In the case of chlorination of ortho chlorotoluene the main products were the 2:4 and 2:3, and a smaller quantity of 2:6-derivative, whilst the presence of 2:5-compound seemed probable but not certain. In the case of the para-compound, the 2:4 is the main product and not 3:4, as found by Miller in the case of bromination.

Considering this difference in the orienting effect of the two halogens we thought it desirable to repeat Miller's work and extend it along the same lines as were followed in the case of chlorination.

Incidentally, we examined the mixed monobromotoluenes—the first product of the action of bromine on toluene—to detect any trace of the meta-compound if formed. We also carried our investigation as far as the tribromo- stage.

In the following table the results of bromination and chlorination are given side by side, the principal product being placed first in each case and a trace indicated by brackets:—

Toluene.	Bromination products. Ortho-, para- (meta).	Chlorination products. Ortho-, para-.
	Monohalogen Compounds.	
Ortho-compound	2:5; 2:4	2:4; 2:3; 2:6; (2:5)
Para-compound	2:4; 3:4	2:4; 3:4
Meta-compound	2:5; 3:4; (3:5)	2:5; 3:4
	Dihalogen Compounds.	
2:3	2:3:6; 2:3:5	2:3:4
2:4	2:4:5; (2:4:6)	2:4:5; 2:3:4; (2:4:6)
2:5	2:4:5; (2:3:5); (2:3:6)	2:3:6; 2:4:5
2:6	2:3:6	2:3:6
3:4	2:4:5; (3:4:5)	2:4:5
3:5	2:3:5	2:3:5

* Read before the British Association (Section B), Birmingham Meeting, 1913.

Attention is directed to the difference produced by chlorination and bromination of orthohaloid toluenes in the orienting effect, which is most marked in the case of the monohalogen compound and the 2:3 and 2:5 halogen derivatives.

A SERIES OF MIXTURES OF NITRO-COMPOUNDS AND AMINES WHICH ARE COLOURED ONLY IN THE LIQUID STATE.*

By C. K. TINKLER, D.Sc.

Whilst engaged in an investigation as to the cause of the colour of certain alkyl iodides of cyclic bases in 1908, it was noticed by the author that in some cases nitro-compounds like these alkyl iodides, when dissolved in fused diphenylamine, gave coloured solutions. In the case of the nitro compounds, however, the colour often disappears on cooling. The investigation in connection with nitro-compounds was not pursued very far at that time, but it has recently been extended.

The most suitable substances for the demonstration of this phenomenon are mixtures of diphenylamine with one of the following nitro-compounds: *o*-, *m*-, and *p*-chlor-nitro-benzene, *m*- and *p*-nitrobenzaldehyde, *p*-brom nitro-benzene, tetra-nitromethane. By enclosing one of these mixtures between two test-tubes placed one inside the other the phenomenon is well demonstrated. Thus, a mixture of diphenylamine and para chlor-nitrobenzene, which is colourless at the ordinary temperature, acquires a reddish yellow colour when held in the hand, and loses this colour when the temperature falls.

A mixture of diphenylamine and *p*-nitro-benzaldehyde shows a deep red colour at 1° above body temperature, returning to the colourless state on cooling. A mixture of diphenylamine and tetranitromethane shows a dark brown, nearly black, coloration, but on cooling in a mixture of ice and salt this colour entirely disappears. On repeating the last experiment several times, however, a permanent green colouring is produced, which is probably due to the decomposition of the nitro-compound. In other cases the mixture undergoes no change on keeping. Thus, a mixture of diphenylamine and *p*-chlor-nitrobenzene prepared five years ago shows the phenomenon as well now as when first prepared.

Attempts to precipitate the coloured substances from solution give interesting results. Thus, by treating a concentrated alcoholic solution of a mixture of diphenylamine and *p*-nitrobenzaldehyde with water a red semi-solid mass is obtained, which, however, on complete solidification, produced by agitation, is perfectly white.

From analogy with compounds of amines and nitro-compounds, such as trinitrobenzene, picryl chloride, &c., prepared by previous investigators, it would appear that the colour of these mixtures under consideration is probably due to the combination of nitro-compound and amine in the liquid state only, and hence various physico-chemical investigations of the fused mixtures were undertaken.

The following results were obtained in this connection:—

1. No evidence was obtained of the separation of a compound in the solid state by cooling a fused mixture.
2. No break was observed in the curve, densities: composition, either in the case of a mixture showing the phenomenon, or in the case of a mixture of trinitrobenzene and diphenylamine where a compound exists in the solid state.
3. A very slight rise of temperature was observed when the fused constituents were mixed.
4. No direct evidence of the formation of a compound was obtained by the determination of the viscosity: composition curve for one of the mixtures showing the phenomenon.

* Read before the British Association (Section B), Birmingham Meeting, 1913.

THE INFLUENCE OF CHEMICAL CONSTITUTION ON THE THERMAL PROPERTIES OF BINARY MIXTURES.*

By ERNEST VANSTONE.

Binary mixtures of compounds of the type Ph α β Ph have been investigated by the method of thermal analysis. Thermal diagrams have been obtained for mixtures of benzoin with each of the following substances:—Benzylaniline, benzylidene aniline, dibenzyl, azobenzene, benzil. hydrazobenzene, benzanilide, and also for mixtures of benzil with each of the following:—Dibenzyl, azobenzene, stilbene, hydrobenzoin, benzanilide. The diagram for benzylidene aniline—benzanilide has also been obtained. In all cases the thermal diagram has a V form, containing one eutectic point. In no case was there any evidence of compound formation, but solid solutions are formed to a limited extent in all cases. For benzoin eutectics both the temperature and concentration of the eutectic mixture is a function of the melting-point of the other constituent. This is seen from the table below:—

Benzoin Eutectics.

Substance.	Melting-point.	Eutectic temp.	Concentration. Per cent benzoin.
Benzylaniline ..	34·2° C.	32·4° C.	3
Benzylidene aniline	49·8	47·0	3
Dibenzyl	51·2	50·2	3·5
Azobenzene	66·2	63·8	6·0
Benzil	94·2	84·0	17·8
Hydrazobenzene ..	130·5	98·4	42
Benzanilide	160·8	116·6	64

The molecular volumes of the various substances have been determined. It is found that at the temperature of the melting-point the unsaturated substance has often a greater molecular volume than the saturated substance. No relation could be found between molecular volumes and eutectic points. Binary mixtures of benzylidene aniline, benzylaniline, stilbene, and dibenzyl with these substances are also discussed.

THE SATURATED ACIDS OF LINSEED OIL.*

By R. S. MORRELL, M.A., Ph.D.

A summary of the literature on linseed oil in Czapek's "Biochemie der Pflanzen," i., 121, and Lewkowitsch's "Oils, Fats, and Waxes" (fourth edition), ii., 50, shows that in addition to the unsaturated acids, linolinic, linolic, and oleic acids, the following saturated acids have been identified:—Palmitic and myristic acids in about equal proportions.

Haller (*Comptes Rendus*, cxlvi., 259, 1906), by fractional distillation of the methyl esters obtained from linseed oil, was able to separate appreciable quantities of palmitic and stearic acids and much smaller quantities of arachidic acid.

The occurrence of stearic acid in linseed oil seemed worthy of further investigation, not only for its practical importance, but also for its relationship to the unsaturated acids present. It is well known that when linseed oil is heated with lead oxide and allowed to cool a solid separates out, whose quantity is increased by addition of petroleum or turpentine. No record of a systematic investigation of this deposit has been published. The lead salts obtained from linseed oil from different sources were freed from unsaturated acids, and yielded a mixture of acid, melting-point 52—54° C., molecular weight 282—3, and iodine value 5—8. The acids consisted of stearic acid, with palmitic acid, and a trace of oleic acid. No myristic or arachidic acids were found. An investigation of the mixture by the methods recommended for the separation of saturated fatty acids has shown that it consists of 68 per cent stearic acid, and the remainder of palmitic acid, with 4·5 per cent oleic acid. The most satisfactory results were given by a combination of the methods devised by Hehner and Mitchell (*Analyst*, 1896, 321) and Kreis and Hafner (*Ber.*, 1913, xxxvi., 2766). The separation of the acids was very tedious, and a much more satisfactory method is desired. When more than two acids are present the quantitative separation is a matter of great difficulty.

* Read before the British Association (Section B), Birmingham Meeting, 1913).

THE

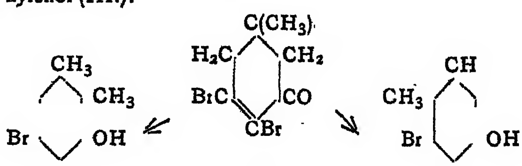
STUDY OF HYDROAROMATIC SUBSTANCES.*

1. *Bromoxylenols obtained from Dimethyldihydroresorcin* (*Proc. Chem. Soc.*, 1912, xxviii., 332).

During the past year work has been largely concerned with the transformation of certain hydroaromatic substances into bromoxylenols. These conversions were originally noticed during the action of phosphorus pentabromide on dimethyldihydroresorcin (*Journ. Chem. Soc.*, 1903, lxxxiii., 110), when the main initial products are not bromoxylenols, but are hydroaromatic in nature, the principal ones isolated being dibromo- and tribromodimethylcyclohexanones.

As the original reaction is very complicated, it was decided to study the transformations using the pure above-mentioned cyclic ketones, and as a result of the work so far concluded it has been established that—

(*a*) The action of heat on dibromodimethylcyclohexenone (I.) gives rise to 5-bromo-*o*-3-xylenol (II.) and 6-bromo-*o*-4-xylenol (III.).

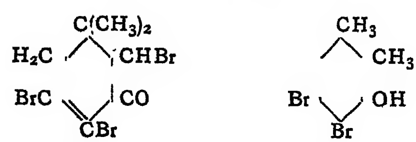


II. I. III.

In the first of these rearrangements a methyl group has wandered, as previously noted, from carbon atom 1 to carbon atom 2; but in the second case from carbon atom 1 to carbon atom 6.

(*b*) The action of dilute alcoholic potassium hydroxide on dibromodimethylcyclohexenone gives rise to 5-bromo-*o*-3-xylenol and 4:5-dibromo-*o*-3-xylenol (V.).

(*c*) Tribromodimethylcyclohexenone (IV.) gives, under the influence of heat or alcoholic potassium hydroxide, mainly 4:5-dibromo-*o*-3-xylenol (V.) and another bromoxylenol, which has not so far been characterised.



IV. V.

The constitutions of 5-bromo-*o*-3-xylenol, 6-bromo-*o*-4-xylenol, and 4:5-dibromo-*o*-3-xylenol have been definitely established by synthetic methods (*Journ. Chem. Soc.*, 1913, ciii.).

* Report of the Committee, consisting of Prof. W. H. Perkin (Chairman), Prof. A. W. Crossley (Secretary), Dr. M. O Forster, Dr. H. R. Le Sueur, and Dr. A. McKenzie. Read before the British Association (Section B), Birmingham Meeting, 1913.

2. *Derivatives of Isopropyldihydroresorcin.*

The method for the preparation of isopropyldihydroresorcin (*Journ. Chem. Soc.*, 1902, lxxxi., 675) has been improved so as to yield 75 per cent of the theoretical amount of the dihydroresorcin.

1-Isopropylcyclohexan-3-ol and 1-isopropylcyclohexan-3-one have been prepared, and it is intended to use them as starting-points for the preparation of several meta-terpene derivatives.

THE STUDY OF PLANT ENZYMES PARTICULARLY WITH RELATION TO OXIDATION.*

THE inquiry has been continued in various directions during the past year, as shown by the following list of communications to the Royal Society:—

(*a*) "Herbage Studies. II. *Lotus corniculatus* and *Trifolium repens*, Cyanophoric Plants." By H. E. Armstrong, E. F. Armstrong, and E. Horton.

(*b*) "Studies on Enzyme Action. XIX. Urease. II. Observations on Accelerative and Inhibitive Agents." By H. E. Armstrong, M. S. Benjamin, and E. Horton.

(*c*) "Studies on the Processes Operative in Solution (XXX.) and on Enzyme Action (XX.). The Nature of Enzymes and of their Action as Hydrolytic Agents." By E. F. Armstrong and H. E. Armstrong.

(*d*) "Studies on Enzyme Action (XXI.). Lipase. III." By H. E. Armstrong and H. W. Gosney.

(*e*) "The *Rôle* of Oxydases in the Formation of the Anthocyan Pigment of Plants." By F. Keeble and E. F. Armstrong (in the "Journal of Genetics").

(*f*) "The Formation of the Anthocyan Pigments of Plants. IV. The Chromogens." By F. Keeble, E. F. Armstrong, and W. N. Jones.

(*g*) "The Formation of the Anthocyan Pigments of Plants. V. The Chromogens of White Flowers." By W. N. Jones.

(*h*) "The Formation of the Anthocyan Pigments of Plants. VI." By F. Keeble, E. F. Armstrong, and W. N. Jones.

Considerable progress has been made in elucidating the part played by oxidising catalysts in the production of plant pigments. By means of suitable agents—in particular benzidine and α-naphthol—oxydases and peroxydases can be localised in plants both in the flower petals and in the vegetative parts. Evidence has been accumulated in favour of the hypothesis that the soluble sap pigments of plants are formed by the oxidation of a colourless chromogen through the agency of an oxydase. The method has been applied with success to certain problems in genetics.

The sap pigment may be reduced to the colourless chromogen by the agency of a reducing substance. Such a change takes place when the coloured cell is stimulated by a hormone (a substance which penetrates the cell membrane) under conditions in which the amount of water present is a minimum. When the conditions are reversed and there is an excess of water in the system, the chromogen is reoxidised. Both the reducing substance and the reduced pigment are soluble in aqueous alcohol of a suitable strength (90 per cent). After extraction of a coloured petal by alcohol of this strength, both the solution and the extracted petal are colourless; but they can be caused to recover their original colour—the solution on evaporation of the alcohol and dissolution of the residue in water, the petal on warming in water. There is evidence that the flower contains an excess of chromogen beyond that normally converted into pigment. The reducing substance is not destroyed by boiling; it cannot therefore be classed as an enzyme. The experiments afford proof of the existence of an oxidising-reducing mechanism in the cell sap which controls the formation of flower colour and is itself regulated by the condition of concentration of the cell sap. Dilution favours oxidation, concentration alters the balance in the opposite direction.

Very little progress has yet been made in determining the chemical nature of the sap pigments. The researches of A. G. Perkin have made it almost certain that the soluble yellow pigments belong to the class of hydroxyflavones of which quercetin is the best known representative. On genetical grounds there is strong evidence in favour of regarding these yellow pigments as antecedents of the red, magenta, and blue sap pigments. By hydrolysis and subsequent reduction and oxidation or by hydrolysis and oxidation, red pigments have been obtained from a number of yellow flowers, such, for example, as the wallflower, daffodil, and primrose; it is possible that the coloured varieties of these species may arise in a similar manner.

The most fruitful discovery during the year has been the proof afforded by Chodat that the action of tyrosinase on an amino-acid, *e.g.*, glycine, gives rise to the production of formaldehyde, ammonia, and carbon dioxide. Elements are thus available for the production of all manner of complex compounds and the method has a wide application. Starting, for example, from a mixture of the glucoside arbutin with glycine, it is possible, by the action of emulsin and an oxydase at the ordinary temperature, to obtain first a red compound, then a brownish black substance, as well as a volatile compound possessing the characteristic odour of ripe plums. In short, both the colour and odour of the ripe fruit are obtained by a biological synthesis from the glucoside and an amino acid. This synthesis appears of general application, and is being further studied. Presumably the colours produced in this manner are those characteristic of the fruit and leaves of the plants rather than of the flower petals. The interaction appears to involve the oxidation of the phenolic constituent of the glucoside either to an *ortho*- or to a *para*-quinone, the condensation to quinhydrone and the interaction of this compound with ammonia and formaldehyde. *Meta*-phenols do not undergo the same transformation.

* Second Report of the Committee, consisting of Mr. A. D. Hall, (Chairman), Dr. E. F. Armstrong (Secretary), Prof. H. E. Armstrong, Prof. F. Keeble, and Dr. E. J. Russell. Read before the British Association (Section B), Birmingham Meeting, 1913.

THE TRANSFORMATION OF AROMATIC NITROAMINES AND ALLIED SUBSTANCES, AND ITS RELATION TO SUBSTITUTION IN BENZENE DERIVATIVES.*

The Transformation of Acylchloroaminobenzenes and the Chlorination of Anilides. The Reactions of Chloroamines in Aqueous Solution. (With W. H. GRAY, B.Sc.).

IN a previous report (*Reports*, 1910) we have given a summary of the results of a large number of experiments on the transformations of chloroamines into the isomeric chloroanilides, Ar.NCl.Ac $\rightarrow$ ClAr.NH.Ac; it was shown that this change could not be regarded as an intramolecular rearrangement, but consisted primarily of a reversible reaction of hydrogen chloride with the chloroamine; thus,—

$$\text{Ar.NCl.Ac} + \text{HCl} \rightarrow \text{Ar.NH.Ac} + Cl_2 \rightarrow \text{ClAr.NH.Ac} + \text{HCl},$$

followed by a direct irreversible interaction of chlorine and the anilide.

In these experiments the medium was aqueous acetic acid containing not less than 50 per cent of acetic acid.

* Report of the Committee, consisting of Prof. F. S. Kipping (Chairman), Prof. K. J. P. Orton (Secretary), Dr. S. Ruhemann, and Dr. J. T. Hewitt. Read before the British Association (Section B), Birmingham Meeting, 1914.

We have now examined the behaviour of acetylchloroaminobenzene in pure aqueous solution, and have discovered an interesting modification of the ordinary reaction.

The production of hydrogen chloride during the transformation of a chloroamine, in the presence of hydrogen chloride, was first indicated by Blanksma (*Recueil des Trav. Chim.*, 1903, xxii., 290), who found that the amount of this acid at the end of the reaction was slightly greater than that originally introduced. Moreover, it was demonstrated by Chattaway and Orton (*Proc. Chem. Soc.*, 1902, xviii., 200) that any change of the chloroamine which occurred in the presence of other acids—for example, sulphuric—was invariably acccompanied by the appearance of hydrogen chloride. The first quantitative experiments were made by Orton and Jones (compare *Reports*, 1910). These were carried out in an acetic acid medium containing from 0—35 per cent of water, both in the presence and absence of various acids. Table I. shows some of the results.

TABLE I.

Medium.	Acid.	Time of reaction	Chloroamine disappeared.	Chloroamine reduced.
Per cent.		Days.	Per cent.	Per cent.
65 HA	None	22	50·8	6·04
"	H_2SO_4	13	49·16	11·2
"	HNO_3	7	54·96	3·72
"	$HClO_4$	9	48·0	18·67

The following experiment serves as a comparison when a chloroamine, which cannot yield an isomeride, is used :—

65 per cent HA H_2SO_4 16 days 8·25 per cent 8·1 per cent

In the following experiments hydrogen chloride (1 molar proportion) is initially present :—

	Per cent.
Glacial puriss. Reaction complete	3·24
Glacial ordinary. Reaction complete ..	6·0
93·4 per cent puriss Reaction complete ..	1·96
75 per cent puriss. Reaction complete ...	1·84

There can be little doubt as to the manner of this reduction. In all aqueous media some hydrolysis of the chloroamine occurs :—

$$Ar.NCl.NAc + H_2O \rightleftarrows HClO + Ar.NH.Ac.$$

The reduction of hypochlorous acid is rapid in aqueous acetic acid even when carefully shielded from light. From an aqueous solution of chloroamine it is possible to distil off hypochlorous acid under reduced pressure. Thus at 25° and under 13·9 mm. the first 50 cc. of distillate from 250 cc. of a 0·1 per cent solution of a chloroamine had a titre of 2·57 cc. of N/20 thio. No chlorine was found in the distillate, and there was no loss of chloroamine from the mother-liquor other than by hydrolysis. The distillation of an equivalent solution of hypochlorous acid showed that the hydrolysis of the chloroamine is not extensive; for the first 50 cc. gave a titre of 30 cc. N/20 thio.

Reduction of the Chloroamine in Aqueous Solution.—The behaviour of acetylchloroaminobenzene in pure water would be expected to show a marked difference from that in concentrated acetic acid media on several grounds. If it be granted that the mechanism of the isomeric transformation consists in a reaction between chloroamine and hydrogen chloride, yielding anilide and chlorine, which then react to form the C-chloro derivative, any extensive hydrolysis of the chlorine should lead to abnormalities and retard the production of chloroanilides. Jakowkin (*Zeit. Phys. Chem.*, 1899), showed that the reversible hydrolysis of chlorine, which is governed by the equation $K[Cl_2] = [HClO][HCl]^2$, is very extensive in dilute aqueous solution. Thus, for example, over 90 per cent of the chlorine at a concentration of 0·05 per cent and less is present as hypochlorous and hydrochloric acids. From the form of the equation it will be seen that the proportion of free chlorine in the system would rapidly increase as the concentration of hydrogen chloride was raised; according to Jakowkin in solutions of hydrogen chloride above 0·1 N very little of the chlorine is present as hypochlorous acid. Above these limits of concentration of hydrogen chloride, therefore, the ordinary conversion of chloroamine would predominate.

Our experimental study is generally in harmony with these anticipations. With a high concentration of hydrogen chloride, the main reaction is a transformation of the chloroamine into monochloroacetanilides, but with low concentrations the reactions are greatly modified. In fact, the behaviour with hydrogen chloride then closely resembles that with other acids.

Aqueous solutions of acetylchloroaminobenzene change very slowly if due regard is had to the purity of the water and the protection of the solution from contamination with reducing materials. At 25° a 0·1 per cent aqueous solution of this chloroamine drops only a few per cent in titre in the course of several weeks; at 60°, however, 50 per cent has disappeared in 38·5 hours. The addition of small quantities of an acid (1 to 2 molecular proportions, which give a concentration of 0·0058 to 0·0116) increases the rate of change, which is, however, still very slow; about 50 per cent of the chloroamine disappears in one month at 25°, but in less than a day at 60°. There is no great difference between different acids, including hydrochloric, in their effect. Careful examination of the reactions, which lead to a fall in titre both in aqueous and highly dilute acids, discloses the fact that the principal change is a simple reduction of the chloroamine to anilide and hydrogen chloride; at the same time a small and very variable amount of chlorate appears. The production of chloroanilides is quite subsidiary. The most obvious interpretation of the facts is that the chloroamine is hydrolysed :—

$$Ar.NCl.Ac + H_2O \rightleftarrows HClO + Ar.NH.Ac,$$

and the hypochlorous acid then reduced. It is not so easy to see how the latter change is brought about. Both an aqueous solution of hypochlorous acid and also solutions containing a strong acid are quite stable. Moreover, the pure anilide does not reduce hypochlorous acid; the sole interaction is the equilibrium represented above. It seems most probable that the reduction is effected by aniline arising from the hydrolysis of the anilide—a change which has been shown to occur, but slowly, under the circumstances. The hydrolysis of the anilide in pure water is yet slower than in acids, and hence the permanence of solutions of chloroamine in this medium at ordinary temperatures. The development of the characteristic colour reactions of aniline with hypochlorous acid in the course of the change is in harmony with this suggestion. Further aniline is particularly effective is a reducing agent for hypochlorous acid, since one molecular proportion reduces several of the acid.

At higher concentrations of the acids (0·023 N) the specific effect of hydrogen chloride appears; but with the other acids the speed of hydrolysis and reduction is merely increased. But even with very great excess of hydrogen chloride, when the disappearance of the chloroamine is relatively rapid, the hydrolysis and reduction can still be detected as a subsidiary reaction. The formation of hydrogen chloride by reduction in the experiments with other acids is the obvious cause, as previously indicated, of the production of the small quantities of chloroanilide.

Method of Experiment.—Aqueous solutions of acetylchloroaminobenzene containing about 1 grm. per litre were used, the reactions being carried out at 25° and 60°. After more than 50 per cent of the chloroamine has disappeared, the hydrogen chloride is estimated. The remaining chloroamine (and the very small amount of hypochlorous acid) is reduced by arsenite, and the chloridion weighed as silver chloride. In order to estimate any chlorate which has been formed from the hypochlorous acid the reduction in another portion is carried out by sulphite. The chloroanilide is assumed to be given by difference, but it is quite possible that some chlorine disappeared in the oxidation of

the aniline or in chlorinating free aniline. Some of the results are shown in Table II.

TABLE II.

Acid.	Temperature.	Percentage of chloroamine converted into— (a) Cl'.	(b) Cl'+ClO$_3$'.	(c) Chloroanilide.
HCl (2 mols.) ..	25°	54·24	8·12	37·64
H_2SO_4 (1 mol.) ..	25°	68·77	12·74	18·52
H_2SO_4 (4 mols.) ..	25°	65·39	15·46	19·14
HNO_3 (1 mol.) ..	25°	76·56	5·59	17·85
$(COOH)_2$ (1 mol.) .	25°	74·36	—	25·64
HCl (10 mols.) ..	25°	12·2	—	87·78
HCl (20 mols.) ..	25°	7·73	—	92·28
HCl (4 mols.) ..	60°	25·42	3·93	70·65
HCl (10 mols.) ..	60°	11·47	—	88·54
HCl (2 mols.) ..	58·5°	43·76	9·36	46·98
Water	60°	63·59	—	36·42
H_2SO_4 (1 mol.) ..	60°	60·85	12·19	26·96
H_2SO_4 (10 mols.) .	60°	73·86	0·91	25·23

The times which the reaction occupies in various cases are very different. The chlorination of the anilide is in an aqueous medium an extremely rapid reaction (Orton and Jones, *loc. cit.*), and hence in circumstances when chlorine and anilide are present at relatively high concentrations, the chloroamine rapidly disappears, and a large proportion of chloroanilide is formed. This condition is realised when the concentration of the hydrogen chloride is sufficiently raised, for, as was shown in the foregoing, the hypochlorous acid is then replaced by chlorine:— $H' + Cl' + HClO \rightarrow Cl_2 + H_2O$, and further hydrolysis of the chloroamine follows from disturbance of the equilibrium: $Ar.NCl.Ac + H_2O \rightarrow Ar.NH.Ac + HClO$.

The time of the half-change in a number of the experiments is shown in Table III.

TABLE III.

Expt.	Acid.	Temp.	Half-period.	Percentage of chloroanilide.
i.	HCl (2 mols.) ..	25°	16·75 days	37·64
ii.	HCl (2 mols.) ..	60°	8·2 hours	43·6
iii.	HCl (4 mols.) ..	60°	2·8 hours	70·65
iv.	HCl (10 mols.) ..	60°	40·5 mins.	88·54
v.	H_2SO_4 (1 mol.) ..	25°	31·5 days	18·52
vi.	H_2SO_4 (4 mols.) .	55°	11·3 days	19·14
vii.	H_2SO_4 (1 mol.) ..	60°	18·7 hours	26·96
viii.	H_2SO_4 (10 mols.)	60°	4·9 hours	25·23

(i.) A comparison of the experiments in which hydrogen chloride was used with that in which sulphuric acid was used at equivalent concentration (i. with v. and ii. with vii.), whether at 25° or 60°, shows that with double the production of chloroanilide, the speed of the disappearance of chloroamine is also approximately doubled.

(ii.) With increase in the concentration of the hydrogen chloride the production of chloroanilide rapidly increases. Raising the proportion of hydrogen chloride from 10 to 20 mols. roughly quadruples the speed, but only slightly raises the proportion of chloroanilide (from 88 to 92 per cent).

(iii.) Increase in the concentration of the sulphuric acid is accompanied by an increase in the rate of disappearance of the chloroamine. But in marked contrast to the effect of hydrogen chloride, the reaction is still identical; the production of chloroanilide and the reduction remain in the same proportion.

These results illuminate some recent observations of Rivett (*Zeit. Phys. Chem.*, 1913, lxxxii., 201) on the "transformation" of acetylchloroaminobenzene in aqueous solution. In one series of experiments he used hydrogen chloride, but never below a concentration of 0·1351. Although the values for—

$$k_I/[HCl]^2 (= 0{\cdot}0413\text{—}0{\cdot}0419)$$

between the limits of 0·2702—0·4797 for [HCl], are very close, he seeks for an explanation of the slightly divergent values outside these limits of concentration only in the degree of ionisation of the hydrogen chloride, and in the secondary influences of the ions on one another or on the unionised molecules on the ions. Our demonstration of the existence of a subsidiary side reaction would indicate another cause for the divergence from strict constancy of the expression $k_I/[HCl]^2$. We have previously attempted (*Reports*, 1910) to show how this relation, $k_I/[HCl]^2 = \text{const.}$, is accounted for on our view of the transformation.

The speed of the formation of chloroanilides is given by the equation:—

$$d[\text{chloroanilide}]/dt = (k_{II}[Cl_2]\ [\text{anilide}] = k_{II}K[\text{chloroamine}][HCl]^2.$$

Since

$$K[\text{chloroamine}][HCl]^2 = [Cl_2][\text{anilide}],$$

from the equilibrium:—

$$Ar.NCl.Ac + H' + Cl' \rightleftarrows Cl_2 + Ar.NH.Ac;$$

hence as chloroamine is the only variable—

$$d[\text{Chloroanilide}]/dt = (k_{II}.K[HCl]^2)[\text{chloroamine}] = k_I[\text{chloroamine}].$$

Apart from the completeness of the ionisation of the hydrogen chloride, and apart from the slight increase in the concentration of the hydrogen chloride during the reaction, the quantity of chloroamine in the equation is supposed to be sensibly identical with that used in the preparation of the system, the reaction with hydrogen chloride being disregarded. These approximations would undeniably cause variation in the expression, $k_I/[HCl]^2$.

The final form of the equation is not changed if the hydrolysis of the chloroamine is taken, as seems necessary in an aqueous medium, as the first step.

$$Ar.NCl.Ac + H_2O \rightarrow Ar.NH.Ac + HClO \text{ and}$$
$$H' + Cl'HClO + ' \rightleftarrows Cl_2 + H_2O.$$

For

$$K_a[\text{Chloroamine}][H_2O] = [\text{anilide}][HClO],$$
$$K_b[Cl_2][H_2O] = [HClO][HCl]^2,$$
$$K_a[\text{Chloroamine}]/K_b[Cl_2] = [\text{anilide}]/[HCl]^2,$$

or

$$K[\text{Chloroamine}][HCl]^2 = [Cl_2][\text{anilide}].$$

In Rivett's experiments with a pure aqueous medium, and also with other acids, he fails to recognise that the transformation of the chloroamine to the chloroanilides is merely a side-reaction, and that hydrolysis and reduction are the primary changes. His measurement of the rate of disappearance of chloroamine in these solutions led him to the conclusion that hydrogen chloride was produced, but he does not determine the amount of hydrogen chloride, and thus misses this fact. Without attempting to examine his views as to the series of changes (reversible) by which he supposes hydrogen chloride to be produced, it may be stated that he does not suggest the reduction of chloroamine or hypochlorous acid. Moreover, it may be pointed out that the pink or purple colour referred to above, which appears during the decomposition of the chloroamine, is without doubt identical with the ordinary colour reaction of bleaching powder and aniline, and not as is suggested due to a compound, $Ar.Nx.Ac$, produced together with hydrogen chloride in a reversible reaction with the acid: $Ar.NCl.Ac + Hx \rightleftharpoons Ar.Nx.Ac + HCl$.

Summary.

1. The decomposition of acetylchloroaminobenzene in pure aqueous solution, or in the presence of all acids including hydrochloric, at a very low concentration is mainly hydrolysis and reduction of the hypochlorous acid:—

$$Ar.NCl.Ac + H_2O \rightarrow Ar.NH.Ac + HClO$$
$$Ar.NH.Ac + H_2O \rightarrow Ar.NH_2 + CH_3.CO_2H$$
$$x(HClO) + Ar.NH_2 \rightarrow (Ar.NH_2 + xO) + xHCl.$$

The transformation of the chloroamine into chloroanilides, which follows from the formation of hydrogen chloride, is quite subsidiary.

2. With higher concentrations of hydrogen chloride, more chlorine appears in the system from the reaction $\cdot H' + Cl' + HClO \rightarrow Cl_2 + H_2O$. According to Jakowkin's measurements, chlorine is nearly completely hydrolysed in water at concentrations below 0·05 in the absence of excess of hydrogen chloride, whilst on the other hand in solutions of hydrogen chloride above 0·1 N, hydrolysis of the chlorine is nearly absent. Hence, now that chlorine and anilide are both at relatively high concentrations, the transformation of chloroamine to chloroanilide is the main reaction.

3. With acids other than hydrogen chloride, increase in the concentration cannot cause a similar change in the reaction.

4. The results of the study of the decomposition of chloroamine in aqueous solution are in complete harmony with the earlier view as to the part played by hydrogen chloride in the conversion of chloroamines to the isomeric chloroanilides.

The Committee asks to be reappointed with a grant of £20.

The Report is a summary of the work which has been carried out. A detailed account of the experimental work will be published later in one of the Chemical journals.

FLAVOUR OF BUTTER INJURED BY METALS.

Economic conditions make it necessary at present to hold butter in storage from the summer season, when it is plentiful, to the winter season, when it is scarce. If the butter is properly made this can be done without materially injuring its quality. It often occurs, however, that butter which has been held in storage for some months develops disagreeable flavours that greatly lessen its value. These bad flavours that will often pass unnoticed when the butter is fresh, may become so serious a defect after three or four months in storage as to render the butter almost unsaleable. The chemical changes which cause these bad flavours are often too small to be detected by the ordinary analytical methods of the laboratory, but the senses of smell and taste are far more delicate, and soon as bad flavours are detected by them the value of the product is lessened.

Some metals either cause or greatly accelerate certain bad flavours in butter, although most of the experiments along this line have not included storage butters. Recently the scientific staff of the Dairy Division of the Bureau of Animal Industry in the United States Department of Agriculture has reported that the presence of very small amounts of iron in cream causes certain undesirable flavours to increase in intensity during storage. These flavours are often designated by butter experts as "metallic," "oily," or "fishy." The injurious effect of iron was found by adding iron in known quantities, varying from 1 to 500 parts, to a million parts of cream. The butter made from such cream was compared with that made from cream where all precautions were taken to avoid any undue contact with iron during the whole process of butter making. The butter was stored at 6° to 10° Fahrenheit, and the quality of the butter was scored by experts at different times. In every instance when the butter was scored a few days after making, the samples to which iron had been added scored lower than the butter made from cream which contained no iron. This held true in most cases on the second and third scoring, which occurred at intervals varying from 20 to 187 days. The most noticeable feature was the rapid development of bad flavour in the butter containing the iron. When both the control and the experimental butter became fishy it was noticed that the control butter was the last to become so. There was a marked oily flavour present in most samples that subsequently became fishy. Only a small proportion of the iron added to the cream was found in the butter, the remainder having been taken up by the buttermilk and wash water.

Butter was also made from cream which had stood in rusty cans, and in every case this butter had a peculiar taste and was easily picked out from all other samples. The buttermilk also had a decided metallic taste.

The influence of copper on the flavour of butter was studied in a similar manner, and it was found that copper, even in small quantities, seemed to cause more marked changes of flavour in butter than did the iron, with a decided tendency toward a fishy flavour in storage. Two experiments showed very plainly the harmful effect of using poorly tinned pasteurisers, even though the cream came in contact with the copper surface for only a few seconds, for, aside from this, all other conditions were exactly alike during the complete process of butter manufacture.

This work shows that if cream is kept in rusty cans or comes in contact with iron or copper at any time during the process of butter making it may take up iron or copper from rusty cans, exposed bolt heads, or other metal parts of pasteurisers or churns, in sufficient quantities to affect the flavour of storage butter. Though there is nothing to show that the nature of the flavour is appreciably changed, it does demonstrate very clearly that the rate of development of the undesirable flavour is greatly accelerated during storage by very small quantities of either iron or copper.—*Chemical Engineer*, xviii., No. 1.

THE SCIENTIFIC WEEK.

(From Our Own Paris Correspondent).

The Supremacy of Iron.

France, who less than thirty years ago occupied an unfavourable rank amongst the producers of iron, has risen during the last few years to one of the first rank. It is especially the increase in the production of the Eastern mining region that raised France from the fifth or sixth place to the third. The mineral production in France in 1912 certainly exceeded a total of 18 millions of tons. The United States holds the world's record with a grand total of 60 million tons. Germany is second with 25 million tons. France comes next, then England, with 16 millions, and Spain with 10 million tons of iron ore. The quantity of iron extracted from the basin of Briey in the Meurthe-et-Moselle district has doubled in less than four years. From 6,000,000 tons in 1909 the production in this region has gone up to 12,000,000 tons in 1912. The department of Meurthe-et-Moselle alone, with its basins of Nancy, Longwy, and Briey, produced in 1912 about 17,000,000 tons of iron ore. All the other mining districts of France scattered from the Pyrenees and Anjou to Normandy produce about 1,000,000 tons. But the production of the basin of Caen will soon, doubtless, be considerably increased. An eminent geologist, M. Bailly, had estimated that the basin of Briey would not reach its normal maximum production before 1970, with a total of 35 million tons. It is probable, however, that this maximum will be reached much sooner. The consumption of sheet iron, iron, and steel is increasing enormously throughout the world. In the struggle that the nations are engaged in for the supremacy of iron, France is well armed. She will easily be able, as soon as she wishes, to take the second rank among the nations of the world.

General Topographical Levelling of France.

The Minister of Public Works is at present undertaking the completion of the third and last general levelling of France. When this operation is finished the total length of levelling will comprise no less than 100,000 kilometres. This gigantic work was undertaken in 1855 by Bourdaloue,

Chief Engineer of the Road-surveying Department, but it is especially since 1884, under the active direction of another engineer, M. Lallemand, that the enterprise has been pushed on with great activity. The general levelling of France included four systems. Their network of meshes, the size of which grows gradually smaller, cover the whole extent of the territory. The first and most important system, called also the basis system, has a development of 1200 kilometres, with meshes of which the circumference varies from 400 to 600 kilometres. Finished in 1892 it was traced with such precision that the initial altitude has been met with again, with only about 6¼ centimetres difference after the whole tour of France had been effected; that is to say, after a distance of 3908 kilometres. It is now fifteen years since the system of the second order has been completed, the meshes vary from 300 to 400 kilometres in width. The system of the third rank is almost terminated; of 47,000 kilometres in length it has meshes of from 60 to 100 kilometres round. Lastly, the fourth and last system has meshes of only 10 to 20 kilometres round. It is expected that it will be completely traced in four or five years time, and thus the general levelling of France will be completed with the utmost precision. This is an occasion to call to mind here that the zero of altitudes that served as a basis for this gigantic operation is to be found at Marseilles. It is placed on the tidal scale, which is fixed on an angle of St. John's Quay, at the foot of the port near the trans-shipping bridge; but what is generally totally unknown is the reason of such a choice. The engineers of the period thought that in the Atlantic, as in the Channel, the average levels, taken in several seaports, did not coincide; that, moreover, the tides might be prejudicial to the determination of this level; that this disadvantage did not exist in the Mediterranean, and that, on the contrary, only very insignificant differences of level had been observed at several points of the Gulf of Lyons. It is at the tidal Observatory of the Corniche that is kept the rivet of iridised platinum that constitutes the fundamental guiding mark for the levelling of the country of France. And the mark is established, naturally, according to the zero of St. John's Quay. That is how it is that, since January 13, 1860, Marseilles has the honour of possessing the zero of altitudes. However, it is now recognised that this measure is somewhat arbitrary. It has been remarked that, following on certain atmospheric conditions, the level of the sea is subject to fluctuations, and that it is materially impossible to trace on any point whatever of the coast a sea level that would be mathematically invariable—that, in a word, would be the average type level.

A Wood that Never Rots.

Engineers have often to deplore the rotting of railway sleepers, of piles, and of wood used to support galleries, in the building of ships, &c. Engineers, chemists, physicists, biologists, doctors, who, for the construction of diverse apparatus, may require a wood possessing a maximum resistance to the causes of destruction, particularly humidity, are interested in this important question of the unputrescibility of wood. The ideal would be to find a wood of a character susceptible of resisting putrefaction naturally. Now it appears from recent researches that the wood of the mangrove tree may be considered as absolutely unputrescible. Numerous samples of mangrove wood (*Rhizophora racemosa*) sent from French Guinea were, in 1909, placed at Collonges (Côte d'Or) in a soaking pit in the depot of sleepers of the Paris-Lyons-Mediterranean Railway Company. The samples were surrounded with all the elements susceptible of producing the decomposition and rotting of the wood in a minimum of time. In spite of these precautions the samples have up till now remained in an excellent state, and show no signs of the least alteration. Why is putrefaction unable to attack the wood of the mangrove? From whence do the particular and excellent qualities of this too little known wood proceed? It is first of all to be remarked that the grain of the mangrove wood is very close; for this reason it opposes a barrier to the invasion of water, by a quasi-mechanical action. To get an idea of the importance of this fact, it suffices to examine comparatively the densities of the woods of the mangrove, oak, and fir. The first is about 110, the second 70, and the third 40. Moreover, mangrove wood has an amount of tannin quite sufficient to prevent the invasion of insects and to prevent the multiplication of germs, damp, mould, and all various micro-organisms which constitute the flora of the woods of different climates. The wood of the mangrove marvellously resists flexion; its resistance is double that of oak, quadruple that of fir; nevertheless, it is not at all brittle. To crushing either at the end or across the fibres it offers a resistance double that of oak and three times that of fir. It resists admirably the efforts of wringing or twisting, far better than the two other woods mentioned, to which it is far superior in suppleness. With these qualities just enumerated it is easily worked; it is as easily sawn as the oak. From the few preceding remarks we may conclude that the wood of the mangrove merits employment on a large scale and for purposes both numerous and varied. Henceforth its use appears to be indicated for the construction of the posts of electric lines on account of its unputrescibility, its resistance, and its suppleness. Its resistance to putrefaction and to crushing render it precious for the construction of sleepers of narrow railways. Its use would be advantageous compared with other woods for the special wood-work of mines, where it would offer all the qualities required by hygiene. And, besides, everyone will find good use for a wood that never rots.

The Ignition of Wood.

The substance the most employed to prevent the ignition of wood is silicate of potassium in solution; the wood is soaked in it, which protects it for a long time from all danger of inflammability. But several successive layers are necessary in order to arrive at a really efficacious immunisation. The following is a good recipe:—35 per cent of silicate of potassium, 35 per cent of sulphate of baryta, from 1 to 2 per cent of zinc white, and lastly 28 per cent of water; but it is not the only recipe. The greater number, however, are trade secrets. M. Wolff considers of great importance the impregnation of the wood with alum in order to render it incombustible; this process, however, does not appear to be in use. It was indeed noticed that during the fire of the alum manufactory of Muskan the fire spared all the beams that had long been exposed to the vapours of alum.

NOTICES OF BOOKS.

An Introduction to the Chemistry of Plant Products. By Paul Haas, D.Sc., Ph.D., and T. G. Hill, A.R.C.S., F.L.S. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1913.

The student of vegetable physiology is but ill-equipped for his work unless he has a knowledge of the elements of organic chemistry, and, moreover, he needs to have a special acquaintance with certain branches which are not usually included in an elementary course. This book is designed to give him this knowledge of the facts and phenomena which are of particular importance in botany, and it is intended to be used after a preliminary course in theoretical and practical organic chemistry. Beginning with the fats and oils and passing on to carbohydrates, glucosides, tannins, &c., the authors describe the preparation, reactions, and methods of estimation of all the commoner compounds. The subject is treated both theoretically and practically, and copious references are given to the literature of biochemistry.

The Synthetic Dyestuffs and the Intermediate Products from which they are Derived. By John Cannell Cain, D.Sc. (Manchester and Tübingen), and Jocelyn Field Thorpe, D.Sc. (Manchester), Ph.D. (Heidelberg), F.R.S., F.I.C. Second Edition. London: Charles Griffin and Co., Ltd. 1913.

In the second edition of this excellent laboratory text-book on the synthetic dyestuffs the general plan and arrangement of the first edition is preserved, the first part giving a theoretical description of the intermediate products and dyestuffs, the second part dealing with their preparation, while in the third part their analysis and identification are discussed, and methods of detecting dyestuffs on the fibre are explained. In this section Green's tables are now reproduced in full, and replace those given in the first edition. The chapter on Oxyketone Dyestuffs is now headed "Anthracene Dyestuffs," and includes indanthrene and similar products, and the new indigoid colouring matters are now treated fully. Many new azo compounds are also described for the first time, and the names of some typical members of the various sub-sections have had to be changed in the new edition.

OBITUARY.

PROFESSOR HUGH MARSHALL.

We regret to have to announce the death of Prof. Hugh Marshall, F.R.S., D.Sc., at the early age of 45.

Prof. Marshall, who was a native of Edinburgh, received his early education in that city, and proceeded from the University there to Munich and afterwards to Ghent. He was appointed Lecturer in Mineralogy and Crystallography at the University of Edinburgh in 1894, and in 1902 he became Lecturer in Chemistry at the same University. In 1908 he was appointed Professor of Chemistry at University College, Dundee. Dr. Marshall devoted himself chiefly to the study of crystallography, and published some important papers on this and allied subjects. He also investigated the metallic salts of some organic acids, and was the joint author of books entitled "An Introduction to Chemical Crystallography" and "Salts and their Reactions." He was elected a Fellow of the Royal Society in 1904.

SIR WALTER HARTLEY.

By the death of Sir Walter Noel Hartley, F.R.S., D.Sc., which occurred on September 11th at Braemar, the Royal College of Science, Dublin, has suffered an irreparable loss, which will be shared by the whole scientific world. Sir Walter Hartley, who was knighted in 1911, was Professor of Chemistry and Dean of Faculty of the Royal College of Science, and was formerly Vice-President of the Institute of Chemistry. In 1903-4 he was President of the Chemistry Section of the British Association, and was a Fellow of King's College, London.

His most famous scientific investigations were in the region of spectroscopy, where he contributed many valuable results of great practical and theoretical importance. He first suggested the employment of an alloy of cadmium, tin, and lead for the purpose of obtaining a spark spectrum which could be used as a standard of comparison, and this alloy has been found to give highly satisfactory results. He also devised a new form of apparatus for obtaining the spark spectra of metallic salts, and made an exhaustive study of the spark spectra of metals and their salts, from which very important conclusions can be deduced. He was a pioneer in the determination of wave-lengths in the ultra-violet region and also in the investigation of the banded spectra of metals obtained in the oxyhydrogen flame. He carried out a long series of experiments on ultra-violet absorption spectra, extending his observations to the case of organic compounds, and publishing his first paper on the subject in the *Philosophical Transactions* in 1879. He conceived the idea of studying the absorption limits of substances at a great many different concentrations, and by plotting the absorption curves deduced from his results he was able to draw very valuable inferences regarding the relation between chemical constitution and absorption spectra. By the use of his method it is possible to determine the molecular constitution of many substances for which chemical methods fail. He investigated the question of the appearance of series of lines in spectra, and studied the relationship between the doublets and triplets in some metallic spectra. He was much interested in the application of photography to the solution of chemical problems, and also published papers on colour changes in some chemical compounds, and on the theory of colour. He was a frequent contributor to the *Philosophical Transactions*, the *Proceedings of the Royal Society*, the *Transactions of the Chemical Society*, and the Chemical News, and wrote a paper which appeared in Kayser's "Handbuch der Spectroscopie" in 1905. He was awarded the Longstaff Medal of the Chemical Society for research in Spectrochemistry in 1906, and the Grand Prix for Spectrographic Research at the Franco-British Exhibition in 1908. He was the author of "Air and its Relations to Life," 1876; "Water, Air, and Disinfectants, 1877"; and "Quantitative Analysis for Students," 1877.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Academie des Sciences. Vol. clvii., No. 1, July 7, 1913.

Acetyl-acetonates of Cerium.—André Job and Paul Goissedet.—Ceric acetyl-acetonate can be prepared by suspending ceric hydrate in water, adding excess of acetylacetone, and shaking. A brown colouration appears, and after several days very dark red crystalline needles separate. They are the normal ceric acetyl-acetonate, CeR_4, with 11 molecules of water. The anhydrous compound may be obtained by evaporating a solution in carbon tetrachloride. It is a black metallic crystalline substance which yields a brown powder when crushed.

Diketones obtained by the Action of Xylylene Dibromides on Isopropylphenyl Ketone and their Decomposition by Sodamide.—M. Dumesnil.—The author has proved that when sodamide acts on diketones or the formula—

$$\mathrm{Ar{-}CO{-}\underset{R'}{\overset{R}{C}}{-}CH_2{-}C_6H_4{-}CH_2{-}\underset{R'}{\overset{R}{C}}{-}CO{-}Ar}$$

diamides are obtained having NH_2 groups in the place of the Ar groups. The diamides can be converted into the corresponding acids by heating with 50 per cent sulphuric acid for six hours in a sealed tube to 150°.

Hydrogenation of α-Ethylenic Secondary Alcohols in presence by Nickel.—Roger Douris.—At a temperature of about 200° propenylisoamylcarbinol, vinylisobutylcarbinol, propenylcyclohexylcarbinol can be hydrogenated over nickel, yielding the corresponding ketones. The saturated hydrocarbons corresponding to the alcohols employed are formed at the same time.

No. 2, July 15, 1913.

Fluorine in the Animal Organism.—Armand Gautier and P. Clausmann.—Fluorine exists in all animal tissues and organs, but in very different amounts, varying from 180 mgrms. to 0·15 mgrm. per 100 grms. of dry matter. It always accompanies phosphorus, to which it appears to be bound. The quantity of it may differ very much in different regions of the same tissue, and it varies with the age of the individual, generally increasing up to maturity, and then decreasing. Muscular tissue is very poor in fluorine, while the blood is relatively rich.

Action of Ultra-violet Rays on Hydrogen Peroxide. —Victor Henri and René Wurmser.—The rate of decomposition of H_2O_2 in monochromatic light is proportional to the concentration, the reaction being monomolecular. For each wave-length it is proportional to the incident energy, and it is also proportional to the energy absorbed, the factor of proportionality being the same for wave-lengths between 2800 and 2060. Einstein's law of photochemical equivalence does not hold good for the decomposition of H_2O_2. The energy absorbed in the decomposition of a grm.-molecule of H_2O_2 is practically equal to the energy liberated by the decomposition of H_2O_2 in the dark.

Additive Reactions of Carbon Monoxide with other Gases under the Influence of the Ultra-violet Rays.—Daniel Berthelot and Henry Gaudechon.—The tendency of CO to give addition products under the influence of light is specially marked with the first members of the different series. Thus it combines with Cl but not with Br or I, with O but not with S, with H_2O but not with H_2S, and with NH_3 and not with PH_3 or AsH_3. These first members are those which have the most important rôle in nature, and the union of CO under the action of light with H, O, H_2O, and NH_3 is of great bio-chemical importance.

Formation of Methane by Catalysis from Carbon Monoxide and Water Vapour.—Léo Vignon.—The following substances act as catalysts, transforming CO into CH_4 in the presence of water vapour:—Al_2O_3, MgO, SiO_2, Fe, Ni, Cu. The mechanism of the transformation differs in different cases. With Fe, Al_2O_3, SiO_2, carbides are first formed, and then decomposed by the water vapour:—

$$12CO + 2Al_2O_3 = C_3Al_4 + 9CO_2,$$
$$C_3Al_4 + 6H_2O = 3CH_4 + 2Al_2O_3.$$

Some hydrogen may also be formed either directly or by the catalysts, according to the equation $CO + H_2O = CO_2 + H_2$. It then acts as follows:— $CO + 3H_2 = CH_4 + H_2O$, $CO_2 + 4H_2 = CH_4 + 2H_2O$.

Lactonisation of α-Ketonic Ethers.—H. Gault.—When pyruvic acid is etherified by ethyl alcohol in presence of HCl, a complex mixture of ethers is obtained. These include ethyl pyruvate, the corresponding acetal, ketovalerolactone carbonic ether, and another lactone ether which is the principal product of the reaction. From the study of the derivatives which this compound forms with hydrazine hydrate and with ammonia the author has proved that it is the ethyl ether-oxide of ketovalerolactone carbonic ether (methylethoxyketodihydrofurfurane carbonic ether).

Action of Sodammonium on True Acetylenic Hydrocarbons.—Paul Lebeau and Marius Picon.—Sodammonium acts on the true acetylenic hydrocarbons of the fatty series to give the sodium derivatives of the hydrocarbons and the corresponding ethylenic hydrocarbon in the proportion of one molecule of the latter to two of the former. Thus with allylene the reaction is $3C_3H_4 + 2NH_3Na = 2C_3H_3Na + C_3H_6 + 2NH_3$. The products obtained in this reaction are very pure, and no secondary reactions have been observed.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xlvi., No. 10, 1913.

Fixation of Atmospheric Nitrogen by Boron Compounds.—Arthur Stähler and John Jacob Elbert.—The reduction of B_2O_3 by means of carbon begins at 1200°, and that of calcium borate (in presence of nitrogen) at 1280°. The yield of boron when fused borax is electrolysed amounts to 12·1 per cent. The authors have shown that calcium boride can probably be prepared from boron oxide and calcium carbide, and have proved that boron nitride begins to give up nitrogen at 2450°. 26—28 per cent of BN is obtained from boron oxide, carbon and nitrogen at 1500—1700°, and under ordinary pressure, while at higher pressures more than 85 per cent BN can be obtained. From boro calcite, carbon and nitrogen at 1800—1400° nearly the theoretical quantity, 46 per cent, of combined nitrogen can be obtained, an increase of pressure having no effect.

Antimony Pentachloride as a Reagent for Aromatic Hydrocarbons.—Siegfried Hilpert and Ludwig Wolf.—A mixture of 1 volume of antimony pentachloride and 2 volumes of carbon tetrachloride is a sensitive reagent for the detection of aromatic hydrocarbons. With pure benzene it gives a yellow or yellowish red coloration, while with commercial benzene the colour rapidly changes to dirty green, and after a time a dark precipitate is formed. Anthracene gives an intense green precipitate, and carbazol a lighter green precipitate. These colorations can be used to test the purity of anthraquinone. All hydrocarbons in which more than one phenyl group is linked to a carbon atom, such as diphenyl methane, triphenylmethane, fluorene, give green addition products, the colours of which are altered if other substituents are present. Thus methyl produces a red tinge, while a nitro-group lightens the colour to yellow or white.

Action of Calcium Hydride on Sulphates.—E. Ebler and K. Herrdegen.—When calcium hydride acts on barium sulphate the following reaction occurs:— $BaSO_4 + 4CaH_2 = BaS + 4CaO + 4H_2$. If 1 molecule of the sulphate to be reduced is mixed with 4 molecules of calcium hydride the reaction begins without any heating; in a few seconds the mass becomes white hot and the hydrogen generated catches fire and burns with a reddish flame. Many sulphates react with calcium hydride, those of heavy metals sometimes yielding the metal. Lead sulphate reacts with explosion.

Atti della Reale Accademia dei Lincei.
Vol. xxii. [i.], No. 8, 1913.

Researches on Aromatic Ketones.—Luigi Alessandri. —When diazomethane acts on phenanthrene quinone gas is evolved, and finally an orange-yellow solution is obtained. From this orange crystalline needles, fusing at 167°, can be separated. Their formula is $C_{15}H_{10}O_2$, and they are formed by the addition of a molecule of methylene to a molecule of ketone, $C_{14}H_8O_2 + CH_2N_2 = C_{15}H_{10}O_2 + N_2$. The substance is stable towards permanganate. When it is boiled with an alcoholic solution of hydroxylamine it is partly converted into two products, the properties of which agree with those of the mono- and dioxime of phenanthrene quinone.

No. 9, 1913.

Influence of Halogens on Phototropism in Hydrazones.—F. Graziani.—The author has studied the phototropism of the hydrazones derived from the three isomeric chlorophenylhydrazines, and has found that none of the o-chlorophenylhydrazones prepared exhibits the phenomenon of phototropism. All of the seven meta-compounds are more or less phototropic, while of the eight para-compounds obtained four were phototropic.

Binary System of Chloride of Lithium with Chlorides of Alkaline Earth Metals.—C. Sandonnini. —Lithium chloride yields solid solutions with magnesium

chloride in all proportions; these solutions are stable at low temperatures. With calcium chloride it also gives solid solutions, which decompose on cooling. With the chlorides of barium and strontium it gives eutectics.

MISCELLANEOUS.

British Association for the Advancement of Science.—The following were the Officers and Committee of Section B (Chemistry) at the Birmingham Meeting of the British Association:—

President—Prof. W. P. Wynne, D.Sc., F.R.S.

Vice-Presidents—Prof. Adrian Brown, M.Sc., F.R.S.; Prof. P. Frankland, Ph.D., M.Sc., F.R.S.; Prof. A. Senier, M.D., Ph.D.; Prof. T. Turner; Mdme. Curie.

Secretaries—E. F. Armstrong, D.Sc., Ph.D. (Recorder); C. H. Desch, D.Sc., Ph.D.; A. Holt, D.Sc.; Hamilton McCombie, M.A., B.Sc., Ph.D.

Committee—Prof. H. E. Armstrong, F.R.S.; Prof. H. Bassett; Prof. P. P. Bedson; Dr. Beilby, F.R.S.; Prof. Bone, F.R.S.; Prof. J. B. Cohen, F.R.S.; Prof. H. B. Dixon, F.R.S.; Dr. J. V. Eyre; Mr. T. Fairley; Prof. A. Findlay; Mr. A. Fleck; Prof. F. Feist; Dr. T. M. Lowry; Dr. A. McKenzie; Dr. R. S. Morrell; Dr. R. H. Pickard; Prof. W. J. Pope, F.R.S.; Dr. T. S. Price; Dr. W. Rosenhain, F.R.S.; Dr. R. E. Slade; Mr. F. Soddy, F.R.S.; Dr. J. F. Thorpe, F.R.S.; Prof. L. Tchugaeff; Sir William A. Tilden, F.R.S.

The Papers brought before the Section were as follows:—

Prof. W. P. WYNNE, F.R.S.—Presidential Address.

Prof. J. B. COHEN, F.R.S., and P. K. DUTT—The Progressive Bromination of Toluene.

Dr. R. S. MORRELL—The Saturated Acids of Linseed Oil.

Dr. C. K. TINKLER—A Series of Mixtures of Nitro-compounds and Amines which are Coloured only in the Liquid State.

E. VANSTONE—Influence of Chemical Constitution on the Thermal Properties of Binary Mixtures.

Prof. W. M. THORNTON—The Influence of the Presence of Gas on the Inflammability of Coal-dust in Air.

H. EHRHARDT—Decomposition Products of Indigo in the Vat.

Reports of Research Committee—(*a*) Hydro-aromatic Substances. (*b*) Aromatic Nitroamines. (*c*) Dynamic Isomerism. (*d*) Plant Enzymes.

Dr. W. ROSENHAIN, F.R.S.—The Amorphous Phase in Metals (with discussion).

Prof. TURNER—The Volatilisation of Metals in a Vacuum.

O. F. HUDSON—The Structural Changes brought about in Certain Alloys by Annealing.

Dr. C. H. DESCH—Further Experiments on Diffusion in Solids.

F. E. E. LAMPLOUGH and J. T. SCOTT—Some Phenomena in the Formation of Eutectics.

Dr. A. HOLT—The Solution of Gases in Metals.

E. VANSTONE—The Electrical Conductivities of Sodium Amalgams.

F. D. FARROW—The System Copper—Oxygen.

R. E. SLADE and G. I. HIGSON—Equilibria of Reduction of Oxides by Carbon.

R. E. SLADE and G. I. HIGSON—The Dissociation Pressures of some Nitrides.

F. JOHNSON—A Study of the Degradation or Enhancement of Quality of Commercial Copper by the presence of Impurities.

Dr. R. H. PICKARD and J. KENYON—Optical Rotatory Powers and Dispersions of the Members of Homologous Series.

Dr. T. M. LOWRY—Rotatory Dispersion.

Dr. T. S. PATTERSON—(1) The Influence of Temperature and Solution on Rotation. (2) Some Suggestions Regarding the Nomenclature of Optical Activity.

Prof. L. TSCHUGAEFF—Anomalous Rotatory Dispersion.

Lieut.-Col. W. GIFFORD—A Partially Corrected Fluor-quartz Lens System for Spectrum Photography.

Dr. J. HULME—Crystalline-liquid Substances.

Dr. BEILBY, F.R.S.—Low Temperature Carbonisation.

Prof. W. A. BONE, F.R.S.—Gas Producers and the Use of Gas.

Dr. R. V. WHEELER—The Composition of Coal.

Dr. M. G. CHRISTIE—Coking and By-product Recovery from Small Coal.

Dr. H. G. COLMAN—The Manufacture of Coal-gas.

J. H. YATES—Gas Fires.

W. H. PATTERSON—The Improvement of Combustion and Blending of Coals.

Dr. R. LESSING—Smokeless Fuel and Coal Oil, and their Relation to Smoke Abatement.

J. F. LIVERSEEGE and A. W. KNAPP—The Action of an Alkaline Natural Water on Lead.

Discussion on Radio-active Elements and the Periodic Law, opened by F. SODDY, F.R.S.

A. FLECK—The Chemistry of the Radio Elements.

Dr. G. HEVESY—Radio-active Elements as Indicators in Chemistry and Physics.

Dr. B. DE SZYSZKOWSKI—(1) Neutral Salt Action. (2) Solubility and Distribution.

Dr. PRIDEAUX—The Hydrogen Ion Concentration of the Sea and the Alkali Carbon Dioxide Equilibrium.

Prof. F. FRANCIS—A New Method for the Determination of Hydroxyl Ion Concentration.

Discussion on Prof. Bragg's Paper on X-Rays and Crystals.

Radio-active Constituents of Sediment of Thermal Springs at Hokuto, Taiwan.—Masataro Hayakawa and Tomonori Nakano.—It has already been observed that the sediment of the thermal springs at Hokuto is radio-active. The sediment consists chiefly of angleso-barytes, but it contains also small quantities (about 0·2 per cent) of cerium and lanthanum. At least three radio-active elements are present in it, viz., ionium, polonium, and radium. The mineral contains no uranium.—*Memoirs of the College of Science and Engineering*, Kyoto Imperial University, v., 4, 137.

Reactions of Ozone with certain Inorganic Salts.—Yoshito Yamauchi.—So far as the author, using a new method of determining the concentration of ozone, could ascertain, ozone is decomposed according to the equation $O_3 = 3O$ only in the case of the oxidation of stannous chloride. The decomposition usually occurs according to the equation $O_3 = O_2 + O$. When ozone acts on sodium thiosulphate two reactions take place, the ozone first causing the catalytic decomposition of the thiosulphate and then effecting the partial oxidation of the sulphite formed. Ozone very rapidly and completely gives thallic oxide with a thallous salt, and a gravimetric method of determining ozone may be based upon this fact.—*Memoirs of the College of Science and Engineering*, Kyoto Imperial University, v., 4, 151.

Proposed International Rubber Congress and Exhibition at Batavia (Java), September, 1914.—The object of the Congress, which will be held from September 7th to September 12th, is the study of the scientific, economical, technical, and commercial questions which concern the rubber culture and industry. Well-known authorities will be invited to contribute dissertations, and the subjects which are best suited for the purpose will, after they have been reported upon, be brought into debate during the Congress. The Secretary of the Committee, Dr. C. J. J. van Hall, Buitenzorg (Java), will willingly supply any information desired concerning the Congress, a definite programme of which will shortly be issued. The Exhibition will be open from September 8th to October 14th, 1914, and will show how the culture and preparation of rubber is conducted in the principal producing countries. Manufactured rubber goods will also be exhibited and sold. Applications for space should be made before November 1st, 1913, to the Secretary General of the International Rubber Congress and Exhibition, Batavia, 1914, Weltevreden (Java), to whom all correspondence concerning the Exhibition should be addressed.

THE CHEMICAL NEWS.

VOL. CVIII., No. 2810.

THE STRUCTURAL CHANGES BROUGHT ABOUT IN CERTAIN ALLOYS BY ANNEALING.*

By O. F. HUDSON, M.Sc., A.R.C.S.

A LARGE number of the useful alloys, particularly those which are rolled, drawn, or otherwise worked, consist of crystals of one kind only—viz., a solid solution. When alloys of this class are annealed, the structural changes that may be observed are:—

1. The cored structure usually characteristic of the alloy in the cast state gradually disappears, and the crystals become quite uniform in composition throughout. Structurally the alloy does not now differ from a pure metal, and other structural changes due to annealing are similar in both cases.

2. If the alloy has been worked before it is annealed pronounced crystal growth is observed when the annealing takes place above a certain temperature, which varies with the alloy. In most cases also numerous twinned crystals are seen. In effect the alloy is recrystallised. If the temperature of annealing is raised the crystal growth becomes more pronounced, particularly from certain centres, and a very coarsely crystalline (overheated) metal or alloy may result. It is, however, to be noted that if the annealing is carried out at a suitable temperature a finer structure than the original is obtained.

The recrystallisation of the strained alloy and the disappearance of the "cores" go on side by side until uniformity of composition is reached.

In the case of alloys consisting of crystals of two or more kinds, those which are malleable are usually composed of crystals of two solid solutions. Generally the chief effect of annealing these alloys is to promote equilibrium between the two phases present. Crystal growth also takes place partly on lines similar to those indicated above and partly by the absorption of the smaller crystals in larger ones of the same kind. In some cases the annealing operation may result in a true recrystallisation. Complete phase and structural equilibrium in some alloys of this class are only attained after very prolonged annealing, and in many instances the alloys as used are in a metastable condition.

The decrease in hardness and the lowering of the elastic limit due to the annealing of cold worked metals and alloys are almost complete before crystal growth becomes noticeable, and are apparently unaccompanied by structural changes which can be observed by microscopical examination.

DIFFUSION IN SOLID SOLUTIONS.*

By CECIL H. DESCH, D.Sc., Ph.D.

SINCE the author's report to the Dundee Meeting of the Association, Bruni and Meneghini have succeeded in demonstrating the occurrence of diffusion in a clear crystalline solid in the case of sodium and potassium chlorides. A mixture of these two salts, heated at 500° or 600°, yields a homogeneous solid solution, the formation of which is recognised by determining the heat of solution in water, which differs from that of a mechanical mixture.

The author's further experiments with metallic alloys show that a sharp boundary is characteristic of diffusion in solids when a chemical compound is formed. An abrupt discontinuity of composition is also observed when one component is removed by solution, as in the dezincification of alloys of copper and zinc.

* Read before the British Association (Section B), Birmingham Meeting, 1913.

THE VOLATILITY OF METALS.*

By Prof. T. TURNER, M.Sc.

CONSIDERABLE attention has been devoted during the past few years to the volatility of metals, especially *in vacuo* or under reduced pressure, and there are considerable possibilities of practical applications in this direction in future. The boiling-points of metals under various conditions as to pressure and atmosphere have been determined by Greenwood and by Kraft, while Berry, Groves, Wair, and the author have investigated the behaviour of metals and of alloys *in vacuo*. Distillation *in vacuo* is specially suitable for volatile and easily oxidisable metals such as sodium, potassium, cadmium, and zinc; lead and bismuth can also be dealt with by similar means. When alloys are heated to suitable temperatures *in vacuo* in certain cases quantitative separation can be readily effected as with the zinc-copper, zinc-iron, and tin-lead series. In other cases, as with the copper-nickel, copper-tin, and copper-iron series, neither metal appreciably volatilises. In some instances definite chemical compounds are obtained. The rate of volatilisation is very markedly affected by the pressure, and to some extent also by the nature of the atmosphere employed. A certain definite or critical temperature s required in order to obtain appreciable volatilisation, and this temperature is raised by gaseous pressure. When this critical temperature has been reached the rate is independent of the initial pressure or the nature of the gas, but varies directly as the increase of pressure. In other words, if the initial rate be R and the rate at any higher temperature to R', then $R' = R + at$. There is an abrupt change in the direction of the temperature curve for equal rates of volatilisation when the pressure reaches 50 mm. of mercury; and at above 80 mm. the curve becomes a straight line. On exhausting it is found that the removal of 1 mm. at from, say, 2 to 1 mm. pressure produces approximately seventy times the effect of the removal of 1 mm. when starting from any pressure above 50 mm.

OPTICAL ROTATORY POWERS AND DISPERSIONS OF THE MEMBERS OF SOME NEW HOMOLOGOUS SERIES.*

By R. H. PICKARD and J. KENYON.

THE authors have synthesised the optically active forms of over 100 compounds belonging to the following ten series:—(1) Methyl alkyl carbinols, Me.CHOH.R, (2) esters of methyl ethyl carbinol and normal fatty acids, MeEt.CH.O.COR, (3) esters of methyl *n*-butyl carbinol $Me(C_4H_9)CH.O.COR$, (4) esters of methyl *n*-amyl carbinol $Me(C_5H_{11})CH.O.COR$, (5) esters of methyl *n*-hexyl carbinol $Me(C_6H_{13})CH.O.COR$, (6) esters of methyl *n*-nonyl carbinol $Me(C_9H_{19})CH.O.COR$, (7) acetates of methyl *n*-alkyl carbinols $Me.R.CH.O.COCH_3$, (8) *n*-dodecoates of the same $Me.R.CH.O.COC_{11}H_{23}$, (9) ethyl alkyl carbinols Et.CHOH.R, (10) *iso*propyl alkyl carbinols $Me_2CHOH.R$. (In each series the "growing chain" is normal and not branched.)

All these compounds possess simple and closely related constitutions, but no numerical relationship between their rotatory powers has as yet been detected. The optical rotatory and dispersive powers of the compounds show well-marked regularities, which are more or less common to all the series. The most pronounced of these is that due to the special stereochemical configuration of that member of an homologous series in which the growing chain (R or —COR in the above formulæ) contains five carbon atoms.

* Read before the British Association (Section B), Birmingham Meeting, 1913.

DYNAMIC ISOMERISM.*

A. *Rotatory Dispersion.*

The past year has witnessed the culmination of an investigation that has a close relationship to the main line of research for which the Committee is responsible. The marked progress that has been made in the study of rotatory dispersion may be shown by the list of papers which have been published during the year. These include a paper on—

"Optical Rotatory Dispersion." Part I. "The Natural and Magnetic Rotatory Dispersion in Quartz of Light in the Visible Region of the Spectrum" (*Phil. Trans.*, 1912, A, ccxii., 261—97),

which will be followed shortly by Part II., in which the extension of the polarimetric method through the ultra-violet and infra-red regions of the spectrum will be described.

The application of these new physical methods to the study of chemical problems is described in a second series of papers, of which the following have been published already, or are in preparation ready for publication in the autumn:—

"The Rotatory Dispersive Power of Organic Compounds."

I. "The Measurement of Rotatory Dispersion" (*Trans. Chem. Soc.*, 1913, ciii., 1062—1067).

II. "The Form of the Rotatory Dispersion Curves" (*Trans. Chem. Soc.*, 1913, ciii., 1067—1075).

III. "The Measurement of Magnetic Rotatory Dispersion" (*Trans. Chem. Soc.*, 1913, ciii., 1322—1331).

IV. "Magnetic Rotation and Dispersion in some Simple Organic Liquids" (*Proc. Chem. Soc.*, June 19, 1913).

V. "A Comparison of the Optical and Magnetic Rotatory Dispersion in some Simple Organic Liquids."

VI. "Anomalous Rotatory Dispersion" (*Proc. Chem. Soc.*, June 5, 1913).

Attention may also be directed to a paper by Armstrong and Walker on "The Causes of Variation in the Optical Rotatory Power of Organic Compounds and of Anomalous Rotatory Dispersive Power" (*Proc. Roy. Soc.*, 1913, A, lxxxviii., 388—403), in which the close relationship between rotatory dispersion and dynamic isomerism is specially emphasised.

The general result of these investigations has been to show that a knowledge of the phenomena of dynamic isomerism is essential for the interpretation of optical rotation, especially in the case of liquids which show anomalous rotatory dispersion; conversely, it is believed that the study of rotatory dispersion will open up a new and fruitful field for the investigation of dynamic isomerism in the case of large groups of important compounds.

B. *Successive Isomeric Changes.*

The past year has also seen the completion of a long series of experiments on the complex isomeric changes which take place in the amide and piperidide of camphorcarboxylic acid. Nearly five years ago it was discovered that these substances were capable of giving inflected mutarotation curves. An investigation of "The Equations for Two Consecutive Unimolecular Changes" (Lowry and John, *Trans. Chem. Soc.*, 1910, xcvii., 2634—2645) showed that inflected curves might be produced by two successive isomeric changes, but the experimental curves were found to be more complex, giving indications of at least three successive changes involving four isomeric compounds. These experiments have been described in detail in two papers published during the past year (Glover and Lowry, *Trans. Chem. Soc.*, 1912, ci., 1902—1912; 1913, ciii., 913—924).

Experiments are now in progress with a view to investigating Forster's α-benzoyl camphor, the enolic form of which has been found to give inflected mutarotation curves when ethylene chloride is used as a solvent in place of chloroform. Even nitrocamphor has been found to give inflected curves if dissolved in ethylene chloride or in benzene (Lowry and Courtman, *Trans. Chem. Soc.*, 1913, ciii., 1216), but it is believed that these are due to the gradual absorption of a catalyst from the walls of the polarimeter tube, and not to successive isomeric changes.

C. *Influence of Light.*

A series of experiments on the influence of light on isomeric change (Lowry and Courtman, *Trans. Chem. Soc.*, 1913, ciii., 1214—1221) has shown that no marked acceleration is produced by exposing nitrocamphor, glucose, galactose, or maltose to the action of powerful ultra-violet light. In the case of aminomethylene camphor, however, very marked acceleration occurs whilst the light is acting, but the action reverts to its original slow rate of change when the light is withdrawn. In the case of (enolic) α-benzoyl camphor a similar acceleration is produced, but the effect continues after the light has been extinguished; it is believed that this permanent stimulation of the action is due to the liberation of benzoic acid acting as a catalytic agent.

* Report of the Committee, consisting of Prof. H. E. Armstrong (Chairman), Dr. T. M. Lowry (Secretary), Prof. Sydney Young, Dr. C. H. Desch, Dr. J. J Dobbie, and Dr. M. O. Forster. (Drawn up by the Secretary). Read before the British Association (Section B), Birmingham Meeting, 1913.

THE ELECTRICAL CONDUCTIVITIES OF SODIUM AMALGAMS.*

By ERNEST VANSTONE, M.Sc.

Continuing the physico-chemical investigation of sodium amalgams, the author has determined their electrical conductivities when in the solid state. The amalgams were melted and drawn up into a capillary spiral 1 mm. diameter, and about a metre in length when unwound. Platinum terminals were sealed in at each end of the spiral.

The liquid amalgam in the spiral was allowed to cool slowly and to solidify in the capillary tube, care being taken to preserve the continuity and uniformity of the thread.

The resistance was measured by a potentiometer method. About twenty amalgams have been examined, the composition varying from 0 to 45 atoms per cent of mercury.

The resistances varied from 0·05 to 0·4 ohm, and the specific conductivities from 18×10^{-4} to $1{\cdot}9 \times 10^{-4}$. The resistances were measured at a temperature of 15° C. The curve obtained by plotting specific conductivies as ordinates and atomic percentages as abscissæ shows two discontinuities and a minimum point. The breaks occur at 85·5 and 77·9 atoms per cent of sodium, and the minimum point at 65 per cent sodium. The thermal diagram has breaks at 85·2, 71·7, and 63·3 per cent sodium.

EQUILIBRIA OF REDUCTION OF OXIDES BY CARBON.*

By R. E. SLADE and G. I. HIGSON.

The equilibrium pressures obtained when certain oxides are reduced by carbon have been determined.

The reaction which takes place is of the type—

$$MO+C \rightleftarrows CO+M$$

where M denotes two equivalents of one of the following substances:—V, Ta, Cr, B, Mn, Sn.

* Read before the British Association (Section B), Birmingham Meeting, 1913).

In some cases a carbide is formed. This reaction is represented by the equation—

$$2MO+3C \rightleftarrows M_2C+2CO.$$

In the experimental method employed there was always an excess of the free metal present. In either case there are three components, M, C, and O, and four phases, CO, M, MO, and either C or M_2C. Therefore, there is one degree of freedom of the system. At each temperature there is a definite pressure of CO.

The substance M was heated in an unglazed porcelain boat *in vacuo*, in the furnace already described by one of us (*Proc. Roy. Soc.*, 1912, lxxxvii., A, p. 519). CO was admitted and reacted with the substance until the pressure had fallen to that of equilibrium. Some CO was then pumped out and the equilibrium attained from the other side.

The upper limit of temperature in some cases was determined by the volatility of the metal, the lower limit of temperature is 800—900° when the reaction—

$$2CO \rightleftarrows CO_2+C$$

begins to take place to some extent. Summary of experimental results :—

	Temperature.	Pressure.
Vanadium	1340°	1·5 mm.
Tantalum	1270°	<0·1 mm.
Chromium	1292°	6·2 mm.
.. .. ..	1339°	9·2 mm.
Tin	750°	>760 mm.
Tin in presence of SiO_3	753°	670 mm.

The values of the equilibrium pressures have also been calculated on the basis of the Nernst heat theorem, and the heats of reaction calculated from the equilibrium pressures when the heats of reaction were not previously known.

THE SYSTEM COPPER-OXYGEN.*

By F. D. FARROW.

THIS paper presented in a concise form the results of the work on the melting-points and dissociation pressures of the system copper-oxygen, obtained by Heyn, Wöhler, and by Slade and Farrow. Heyn has obtained melting-points of mixtures containing up to 1 per cent of oxygen. He finds a eutectic point with an oxygen content of 0·39 per cent at 1065° C., while the mixture containing 1 per cent of oxygen melts at 1167° C.

Slade and Farrow have shown that mixtures containing between about 2·3 and 10·3 per cent of oxygen when heated above 1195° C. melt and form two liquid layers, the upper of which is richer in oxygen than the lower. The composition of these layers is for all temperatures investigated about 2·3 per cent of oxygen for the lower and about 10·3 per cent for the upper. The compositions do not appear to approach each other with rising temperature. By extrapolating over a short distance the authors place the melting-point of cuprous oxide (11·26 per cent of O) at 1210° C.

The same authors have investigated systems whose composition lies between those of cuprous and of cupric oxide. They find two melting-point curves which intersect at about 1060° C. The eutectic mixture corresponding to this has a composition of 14·8 per cent of oxygen. The melting-point of cupric oxide is found not to have been attained at a temperature of 1148° C., at which temperature the dissociation pressure of the oxide exceeds 2½ atmospheres.

Wöhler has determined the dissociation pressures of cupric oxide when heated. He has shown that solid solutions of cuprous oxide in cupric oxide are formed. His values therefore are somewhat lower than the highest dissociation pressures obtainable.

Slade and Farrow have determined the dissociation pressures of cuprous oxide at temperatures and under conditions at which the mixture of two liquid phases mentioned above must necessarily have been present. These pressures are given in the subjoined table as points on the experimental curve *c g*.

From the sources mentioned the data have been collected and used to construct a temperature-composition and a temperature-pressure diagram which are attached to the paper.

Table of Numerical Values of the Data Represented by the Chief Points on the Diagrams.

Name.	Temperature Centigrade.	Composition =oxygen content per cent.	Pressure.
a	1084	0·0	—
b	1065	0·39	—
c	1195	2·26	—
d	1210	11·16	—
e	*c.* 1060	*c.* 14·8	*c.* 460 mm.
f	?*c.* 1240	20·10	? 20 atm.
Curves.			
m e	960	—	50 mm.
	1050	—	314 mm.
	1070	—	458 mm.
c g	1205	—	4 mm.
	1240	—	10 mm.
	1260	—	12 mm.
	1324	—	25 mm.

Explanation.

(*a*) Melting-point of pure Cu.
(*b*) Cu, Cu_2O eutectic.
(*c*) Invariant point. Phases present: Solid Cu_2O, liquid I. Liquid II. Gas.
(*d*) Melting-point of pure Cu_2O.
(*e*) Cu_2O, CuO eutectic.
(*f*) Melting-point pure CuO.
(*m e*) Wöhler's curve of CuO dissociation pressure.
(*c g*) Slade *v.* Farrow's curve of dissociation pressure of the two liquid phases of the Cu_2O, Cu mixture.

A STUDY OF THE

DEGRADATION OR ENHANCEMENT OF QUALITY OF COMMERCIAL COPPER BY THE PRESENCE OF IMPURITIES.*

By FREDERICK JOHNSON, M.Sc.

IN this paper the author surveyed the facts and theories which have been brought to light of late years by modern scientific investigation of the influence of traces of impurities upon the chemical, physical, and mechanical properties of copper. Much of the mystery formerly attaching to defects during manufacture and failures in service has been cleared up, to the benefit alike of the manufacturer and the user. Ancient and modern prejudice against the presence of impurities such as oxygen and arsenic has been shown to have no foundation in fact when certain uses of the copper are considered.

The knowledge of metallurgical testing and analysis was shown to be indispensable when the varying composition of commercial brands of crude copper and the multitudinous uses to which refined copper is put are taken into consideration.

Manufacturers should never lose sight of such fundamental considerations as the following :—

* A Paper read before the British Association (Section B), Birmingham Meeting, 1913.

* Read before the British Association (Section B), Birmingham Meeting, 1913.

1. To what degree the various impurities may be eliminated during refining operations.

2. To what specifications (however imperfect such specifications may be) the resulting changes may have to conform.

3. To what extent impurities may mutually react to the improvement or detriment of the resulting material.

The author has given special attention to the influences of oxygen and arsenic, whilst bismuth, lead, nickel, antimony, silicon, iron, phosphorus, manganese, &c., are all dealt with in turn.

The evidence of the microscope is called largely into requisition and the importance of various kinds of testing is emphasised.

THE

DISSOCIATION PRESSURES OF SOME NITRIDES.*

By R. E. SLADE and G. I. HIGSON.

THE dissociation pressures of the nitrides of vanadium, tantalum, and boron have been investigated.

The substance was heated in an unglazed porcelain boat *in vacuo*, in the furnace previously described by one of us (*Proc. Roy. Soc.*, 1912, lxxxvii., A, p. 519). Nitrogen was admitted and was absorbed by the substance to form nitride until the dissociation pressure was attained. Some nitrogen was then pumped off and the equilibrium attained from the other side.

Summary of experimental results:—

	Temperature.	Pressure.
Vanadium ..	1203°	Not greater than 0·2 mm.
..	1271°	Not greater than 1·5 mm.
Tantalum ..	1170°	0·4 mm.
Boron	1222°	Not greater than 9·4 mm.

The results are discussed from the point of view of the Nernst heat theorem.

ROTATORY DISPERSION.*

By T. MARTIN LOWRY, D.Sc.

ATTENTION was directed to the importance of making measurements of optical rotation over a range of wavelengths, instead of merely with light of one colour. This is specially necessary in the case of substances, such as derivatives of tartaric acid, in which anomalous rotatory dispersion is known or may be suspected to exist.

After experiments extending over a period or seven years, the methods of measuring rotatory dispersion have been so simplified that they are now within the range of the ordinary advanced student, and should soon become a regular part of the ordinary routine of the laboratory. For many purposes it is sufficient to take readings with the green and violet mercury lines, but sodium and lithium may also be used in order to see whether the curve of rotatory dispersion has the normal form. A still more valuable check is provided by readings taken with the red and green cadmium lines, but these require more complex apparatus and cannot yet be regarded as generally available.

The examination of the optical and magnetic rotatory dispersion of some fifty organic liquids has shown that the curve of rotatory dispersion has an extremely simple form. It can be expressed by the equation

$$\alpha = \frac{k}{\lambda^2 - \lambda_0^2}$$

where k is the "rotation constant" and λ_0^2 the "dispersion constant" for the substance. If α is plotted against λ_0^2 the curve is a simple rectangular hyperbola, tending to a limiting value $\alpha = 0$ when $\lambda^2 = \infty$ and to $\alpha = \infty$ when $\lambda^2 = \lambda_0^2$. If $\frac{1}{\alpha}$ is plotted against λ^2 the curve becomes a straight line. In the case of substances, such as ethyl tartrate, which show anomalous rotatory dispersion, two of these terms must be employed thus:—

$$\alpha = \frac{k_1}{\lambda^2 - \lambda_1^2} - \frac{k_2}{\lambda^2 - \lambda_2^2}$$

This is in accordance with Biot's view that anomalous rotatory dispersion is produced by the admixture of two substances differing in rotatory dispersive power as well as in the sign of their optical rotations.

ON ANOMALOUS ROTATORY DISPERSION.*

By L. TSCHUGAEFF.

1. THERE are three different types of anomalous rotatory dispersion. The anomaly in question may be due: (*a*) To the superposition of two (or more) different kinds of normally dispersing molecules, differing in rotatory dispersive power as well as in the sign of their rotation. This type of anomalous dispersion was first established by Biot. (Ex. mixture of *l*-menthone and *iso*-menthone.) (*b*) To the existence of absorption bands in the spectrum of the active substance, as it has been pointed out by Cotton, Drude, and others. (Cotton's phenomenon.) (Ex. the xanthates and thiourethanes of menthol, borneol, and fenchol.) (*c*) To the *intramolecular* superposition of partial rotations corresponding to several centres of activity of one and the same molecule, as it has been shown first by the author. Experimental evidence in favour of this classification is given.

2. It has been established that the shape of the dispersion curve is largely influenced by constitutive factors, and in the first place by the relative position of the centres of activity and of the chromophor groups within the active molecule, the whole dispersion curve resulting from the superposition of several "partial" curves. These results are discussed from the point of view of the electronic theory.

3. The influence of the temperature and the nature of the solvent on the rotatory dispersion of the optically active xanthates resembles closely the influence exerted by the same factors on the dispersion of tartaric acid and of its ethereal salts as studied by Winther and others. There must therefore be an intimate analogy in the origin of the anomaly in both cases.

RADIO-ELEMENTS AS INDICATORS IN CHEMISTRY AND PHYSICS.*

By G. HEVESY, Ph.D.

BY means of an α-ray electroscope of ordinary sensitiveness it is possible to measure accurately as small a quantity as 10^{-17} grms. of a radio-active substance having a half-value period of one hour. The extraordinary simplicity and at the same time sensitiveness with which it is possible to measure these extremely small quantities of radio-active bodies makes them of the greatest use not only in studying substances in great dilution but also as indicators of physical and chemical processes.

Radio-active indicators may be conveniently divided into two principal groups. To the first group belong those whose use as indicators depends only on their physical properties and not on their chemical properties. Some

* Read before the British Association (Section B), Birmingham Meeting, 1913.

* Read before the British Association (Section B), Birmingham Meeting, 1913.

examples of the use of radio-active indicators of this kind are the following:—

It is only necessary to know that the radio-elements composing the active deposits are metals in order to test the formula of Arrhenius connecting the variation of velocity of solution of metals in acids with the temperature. This has been lately carried out by Miss Ramstedt.

It is known from the kinetic theory that the concentration of a solution varies with time, and this problem, which could not be attacked by ordinary methods, has been made experimentally feasible by the use of radio-active bodies as indicators. (Svedberg, Smoluchowski).

The existence of colloidal solutions of radio elements has been lately established by Paneth and Godlewski, and experiments have been undertaken on the formation and precipitation of these colloids using radio-active indicators.

The emanations, the only gaseous radio-elements, have been employed to establish the validity of the gas laws, especially that of Henry's law for extremely small partial pressures. (Bruhat, Boyle).

Fick's Diffusion Law has also been shown to hold accurately for bodies in infinitely small concentration by making use of radio-active substances.

It is often a question of practical interest to the chemist to know how often it is necessary to wash out a pipette or a beaker in order to remove the last trace of the solution it had contained. This problem can be investigated with extreme ease when radio-active indicators are used.

The fact, however, that most radio-elements are throughout in all chemical properties exactly similar to some of the common elements (for instance, radium D and thorium B are non-separable from lead, thorium C and radium E from bismuth, &c.) allows these bodies to be used chemically as indicators of the bodies from which they are known to be non-separable. Radium E can be used as an indicator for bismuth, radium D for lead, &c.

If 1 mgrm. of lead is mixed with a quantity of radium D which gives 10,000 units of activity in an electroscope, one-millionth part of this mixture is easily detectable by the radio-activity of radium D. In this way 10^{-6} mgrms. lead is quantitatively determinable.

By this method also the solubility of the difficultly soluble salts of lead, such as the chromate and the sulphide, has been determined. Further, the amount of lead chloride entrained by a precipitate of silver chloride after washing the latter thoroughly with water is measurable.

Experiments on the electrochemical behaviour of small quantities of lead and bismuth have been begun. By means of these indicators a study may be made of the electrochemical behaviour of these metals for electrode potentials lying below the decomposition voltage, a problem which could not be investigated by any other means.

Of especial use are the indicators for investigating the diffusion and mobility of ions in extremely small concentration, from which results we obtain information concerning the behaviour and the hydration of ions in very dilute concentration. Data are already available on the diffusion rate of lead salts down to a normality of 10^{-14}.

THE ROTATION OF ACTIVE COMPOUNDS AS MODIFIED BY TEMPERATURE, COLOUR OF LIGHT, AND SOLUTION IN INDIFFERENT LIQUIDS.*

By T. S. PATTERSON, D.Sc. Ph.D.

BEFORE it can be possible to offer a real explanation of the phenomena of optical activity, attention must be devoted to the lowlier task of trying to understand clearly the main features of the phenomena in question; to study carefully, in fact, what may be termed the morphology of the subject. The variation of rotation with change in the colour of light, with change of solvent, with change of temperature, and perhaps even with change of pressure, must be thoroughly examined.

As regards the last little can be said, but the other three —colour of light used, the nature of the solvent, and the temperature—are of the utmost importance. Even the data available at present seem sufficient to give some idea of the general behaviour of optically active compounds with changes of condition, and this may be summed up into one scheme, as follows:—

It has been found that the rotation of certain active compounds reaches a maximum value at a certain definite temperature. Further, points of inflection often occur in temperature-rotation curves, sometimes in such as show also a maximum, and by piecing together the evidence collected from an examination of a fair number of optically active substances it seems probable that the variation of the rotation of an active substance with change of temperature may be, and very probably is, a periodic phenomenon, doubtless irregularly periodic—such that several maxima and minima may be expected to occur in the curve representing it. Owing to experimental difficulties, however, it is not possible to trace these curves through any very wide range of temperature.

Now it seems legitimate to assume that a point of maximum rotation indicates that condition of the substance in which one of the groups attached to the asymmetric atom attains to a maximum influence—a singular condition of the substance. When such singular points are found in the curves of condition for a number of fairly closely related compounds it seems reasonable to suppose that the maxima represent the rotations of these different compounds in, at least, fairly similar conditions. The great merit of a maximum rotation is its recognisability and the possibility it affords of tracing some particular state of the compound as the external conditions are varied. Maxima are found at different temperatures for the various members of a homologous series, but the discussion of this field, since it involves the relationship between the rotation and the constitution of a series of active compounds, may be passed over until the variation of rotation of a single active compound with change of external conditions is more fully understood.

Here the first matter to which attention may be directed is that the maximum, in certain cases at any rate, occurs at a different temperature for light of various refrangibilities, whence it would appear that the irregularly periodic temperature-rotation curves are probably retarded on each other; and since the curve for violet light has the greatest amplitude, it follows that these curves cut one another throughout a certain region, and in this region the rotation-dispersion of the substance must necessarily be anomalous. Hence we arrive at once, not, it is true, at an explanation of anomalous rotation-dispersion, but at a reason why anomalous rotation-dispersion should exist at all.

It is doubtful whether any substance will really show normal rotation-dispersion, but if such a substance be found then it seems probable that the temperature-rotation curves for the different colours of light will intersect at a single point, the rotation-dispersion being positive on one side of this point and negative on the other.

Rotation in Solution.—A study of such data as are available appears to show that when such a compound as shows a maximum rotation—for example, ethyl tartrate—is dissolved in some indifferent liquid, this maximum rotation is displaced towards a lower or a higher temperature, as the case may be, with a corresponding alteration in value, solvents differing very much in regard to the displacement which they bring about. Now it is also found that the region in which abnormal rotation-dispersion takes place is shifted, on solution, in a very similar way to that in which the maximum rotation is displaced, and therefore it seems clear that the effect of solution is to displace the whole temperature-rotation curve. It then appears at once why some substances which show abnormal rotation-dis

* Read before the British Association (Section B), Birmingham Meeting, 1913.

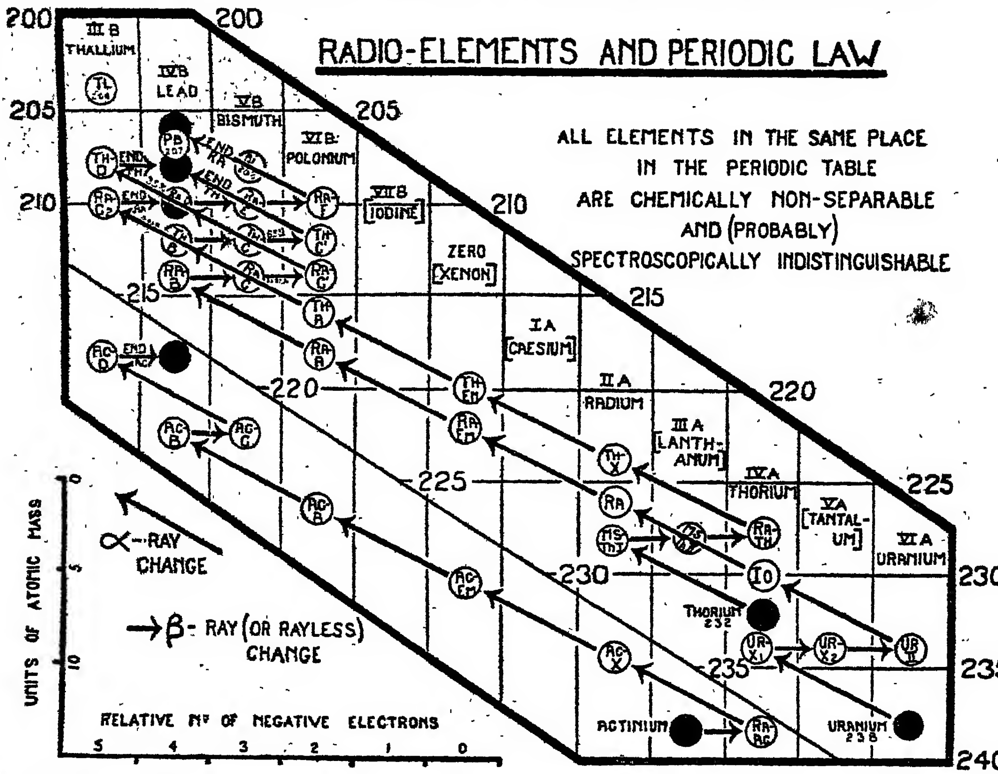
persion at a certain temperature for the homogeneous compound show a normal rotation-dispersion when dissolved in some solvent which considerably alters the rotation. The solvent has the effect of shifting the family of temperature-rotation curves in such a manner as to bring the parts of the curves in the neighbourhood of the maximum into view, and in this neighbourhood the rotation-dispersion appears to be normal.

THE RADIO-ELEMENTS AND THE PERIODIC LAW.*

By FREDERICK SODDY, M.A., F.R.S.

During the present year, 1913, the general law governing the passage through the periodic table of the elements in process of radio-active change has been discovered. As the result it is possible to write the three disintegration series of uranium, thorium, and actinium across the periodic table, so that each member falls into its proper place in the case of the twenty-seven members the chemistry of which is known. For the six members the period of average life of which is too short for the chemical nature to be determinable, and for the five inactive end-products, the chemical nature can be without uncertainty predicted. The general law is that an α-ray change, when a helium atom carrying two atomic charges of positive electricity is expelled, the element changes its place in the periodic table in the direction of diminishing mass and diminishing group number by two places. In a β-ray change, when a single atomic charge of negative electricity is expelled from the atom as a β-particle, and also in the two changes for which the expulsion of rays has not yet been detected, the element changes its position in the table in the opposite direction by one place.

The generalisation as regards the α-rays was put forward in 1911 (Soddy, "Chemistry of the Radio-Elements," p. 29), but at that time the chemistry of the β-rays giving members, which are mostly short-lived, was not known well enough for anything definite to be said. Fleck in 1911 commenced to make a systematic investigation of the chemically indefinite members, from the point of view adopted in the book referred to, of the existence of chemically identical and non-separable groups of elements. This work occupied two years. Some of the results were communicated to this section at the Dundee Meeting last year, and they have now been published in the Journal of the Chemical Society (*Proc.*, 1913, xxix., pp. 7, 172; *Trans.*, 1913, ciii., pp. 381, 1052). It is important to note that this work was purely experimental, and was done deliberately without any attempt to find the theoretical law, in order that the results might be free from all bias in favour of any particular view. It would have been easier to speculate first and then to test the speculations, but the opposite course was purposely adopted.



Fleck, in addition to confirming the chemical nature of several of the chemically better known members by careful fractionation methods, had by the beginning of this year succeeded in elucidating the chemical nature of nine members which had not previously been elucidated. All except two of these were in the series subsequent to the zero or emanation group, of which members only the two longest lived—polonium and radio lead—had previously been chemically characterised. At this time A. S. Russell (Chem. News, January 31, 1913, cvii., 49), who knew of Fleck's results, put forward the view that in the β-ray change the position of the element in the periodic table changes by one place, and he was the first to publish a complete scheme showing the passage of the radio-elements through the periodic table. His scheme was in

* Abstract of Paper opening the Discussion. British Association, Birmingham Meeting (Section B).

certain respects imperfect, and it was followed almost immediately by another by K. Fajans (*Phys. Zeit.*, February 15, 1913, xiv., pp. 131, 136), who put forward the complete law in its present form, and made important and accurate deductions as to the positions occupied by the still unplaced members. Soddy independently arrived at a complete scheme similar to that of Fajans (CHEM. NEWS, February 28, 1913, cvii., 97), but which in one respect possibly went somewhat further in regard to the generalisation that all elements falling into the same place in the periodic table are not merely similar in chemical properties, but are chemically identical, non-separable by chemical methods, and probably spectroscopically indistinguishable. From this the definite prediction was made that radium-C_2, thorium D, and actinium-D would prove to be non-separable from thallium, and radium A from polonium, which Fleck has since established, whilst all the end-products would be non-separable from lead. The scheme, altered slightly to bring it up to date (July, 1913), is shown in the accompanying plate.

In all three schemes a new member was indicated in the V.A family, as the product of uranium X. This has since been discovered by Fajans and Beer (*Naturwissenschaften*, April 4, 1913), and confirmed by Fleck (*Phil. Mag.*). It proves to be a very short-lived substance of period of average life 1·7 minutes, and is called Uranium X_2. Its parent, Uranium X_1, with period 35·5 days, gives only the soft (β) rays, whereas the hard β-rays of uranium X come from this new product.

This missing member being short-lived disproves the suggestion (Soddy) that it might be a very long-lived and and therefore well-defined element (Eka-tantalum), disintegrating dually, and producing, in addition to uranium II. by a β-ray change, actinium by a still undetected α-ray change. This being disproved, the only other possibility to consider as to the still unknown source of actinium is that it is produced in a β-ray or rayless change from radium. On account of the uncertainty of the origin of actinium, and therefore of the atomic weight both of itself and of all its products, the actinium series is shown separately beneath the others in the plate.

The chemical analysis of matter is thus not an ultimate one. It has appeared ultimate hitherto, on account of the impossibility of distinguishing between elements which are chemically identical and non-separable unless these are in the process of change the one into the other. But in that part of the Periodic Table in which the evolution of the elements is still proceeding, each place is seen to be occupied not by one element, but on the average, for the places occupied at all, by no less than four, the atomic weights of which vary over as much as eight units. It is impossible to believe that the same may not be true for the rest of the table, and that each known element may be a group of non separable elements occupying the same place, the atomic weight not being a real constant, but a mean value, of much less fundamental interest than has been hitherto supposed. Although these advances show that matter is even more complex than chemical analysis alone has been able to reveal, they indicate at the same time that the problem of atomic constitution may be more simple than has been supposed from the lack of simple numerical relations between the atomic weights.

Hydrolysis of Levulosanes.—Ph. L. de Vilmorin and F. Levallois.—In the hydrolysis of inulin sulphuric and oxalic acids gives results which are too variable to serve as a basis for a method of analysis. Acetic acid used at a temperature of about 80° and a concentration of 3 to 10 per cent is accurate, but as the temperature is raised the results obtained become rather too high. Very small quantities (0·72 to 4·3 grms. per litre) of sulphosalicylic acid at temperatures varying from 80° to 100° give accurate results.—*Bull. Soc. Chim. de France*, xiii.-xiv., No. 13.

ON THE

CRYSTALLINE DEPOSIT OCCURRING IN THE TIMBER OF THE "COLONIAL BEECH" (*Gmelina Leichhardtii*, F.v.M.).*

By HENRY G. SMITH, F.C.S.

THIS Australian tree belongs to the Family Verbenaceæ, and is thus not a true "beech." The use of this common name for *Gmelina Leichhardtii* is an unfortunate one, as it really belongs to the genus *Fagus* of the Cupuliferæ. The tree is a native of New South Wales and Queensland, and grows to a considerable size, reaching to a height of 100 to 150 feet, with a diameter of over 3 feet. It is a useful commercial timber, light in colour, but with little or no figure, and thus cannot be classed as ornamental, although it is useful for carving and similar art purposes.

The seasoned timber often has white particles filling the cells of the wood, and these are sometimes so plentifully distributed that the planed surface has the appearance of having been filled, to a certain extent, with a substance like plaster-of-paris. When the timber is not sound this substance often accumulates in "shakes" and cracks of the wood as small opaque deposits, and in crystalline masses. Under the microscope these masses were seen to consist of needle crystals.

The presence of some substance in "beech," different from that of other native timbers, has previously been observed by saw-millers, and in a letter from Mr. W. Smith, of Tinnonee, New South Wales, he refers to this peculiarity as follows:—"Port Macquarie Beech contains something of a very cleansing nature. We have a planing machine, and, of course, it gets dirty, and stuck all over with sap and dust from tallow-wood and other hard woods, but as soon as we have put through a few beech boards, wherever the sappy chippings strike, the ironwork of the machine becomes clean and as bright as new."

Another saw-miller also mentioned that he had seen whitish deposits in "beech" timber, but thought them to be a fungoid growth.

The first well-defined deposit of this substance came into the possession of the Technological Museum a few years ago, and as much work as possible was, at that time, carried out with it, a crystalline body being isolated, and its melting-point determined. About two years later a small quantity was received from another locality, and similar crystals were again isolated from it, and found to be identical in appearance with the first, and to melt at the same temperature. Through the kindly assistance of Mr. Breckenridge, a Sydney timber merchant, a portion of a beech log in a very unsound condition was recently obtained from which a few grms. of pure crystals were extracted, sufficient to enable a more extended investigation to be undertaken.

The crystals obtained from all the trees from the various localities were colourless, odourless, and tasteless, and were identical in crystalline form, in melting-point, in optical activity, and exhibited the same peculiarity in the melting-points of the substance when in either the crystalline or the amorphous conditions. From this it is apparent that the deposit is a common constituent in the timber of this species of *Gmelina*, and also that it is a definite chemical substance. It is possible that it may be characteristic of this tree, or perhaps peculiar to the genus, and if so, its identification would become of some assistance towards correct diagnosis, especially as no other body appears to be present in the deposit which might contaminate it, and thus interfere with the ready isolation and purification of the crystals.

The peculiarity of this body in what appears to be perhaps an example of dynamic isomorphism in a natural chemical

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* A Paper read before the Royal Society of New South Wales, November 6, 1912. From the *Journal of the R. S. of New South Wales*, 1912, xlvi., 187.

substance, shown by its varying melting-points under different conditions, has made its study somewhat interesting, and, so far as the material at disposal would allow, considerable work has been done with it.

The following data will show how great were the differences between the melting-points of the crystals and those of the same substance after melting :—

(*a*) When the crystals were prepared by crystallisation from alcohol, or from boiling water, they were quite anhydrous, and melted at 122° C., to a transparent resin-like body, without alteration in weight. This fused material was, at first, strongly electric, and had the power of attracting light particles of filter-paper, &c., very energetically. The melting-point of this glassy substance had, by fusion, been reduced to 62—63° C., and so long as it remained in the glassy condition in the lump, the melting-point did not rise, even after many weeks, but if the fused substance was powdered the melting-point commenced to rise at once, and after a comparatively short time this had reached about 120—121°, but did not appear to revert quite to the melting-point of the original crystals.

(*b*) When the fused substance was powdered and the melting-point taken at once, this powder melted at the same low temperature as the spangles of solid material, but if the temperature was continually raised, when this had reached to about 100°, the melted substance became somewhat opaque, but reverted again to the transparent condition at the melting-point of the original substance.

(*c*) When the original crystals were boiled in water they softened and apparently fused at that temperature, and, when the solution had become saturated, remained as fused globules or masses in the boiling water, but soon solidified into a semi-crystalline condition when the water had sufficiently cooled, showing that complete fusion had not taken place, because when fused by dry heat the mass always remained as a glass, and there was no sign of crystallisation during the many weeks it remained under observation. If, however, this glass was dissolved in alcohol it again readily crystallised from this solvent, and the crystals were also readily formed from water when the glassy form was boiled directly in the usual way. When thus re-crystallised, the melting-point of the crystals, both from the alcohol and from the water, had reverted to that of the original crystals, although the melting-point of the fused material from which they had been derived had only been 62—63°.

(*d*) If the melted glassy substance was broken up into small spangles, but not powdered, these became, after several weeks, opaque and yellowish in colour. The melting-point of these opaque spangles had then considerably increased, showing that the tendency is to revert to the higher melting-point in all cases, which may thus be considered the stable condition. How many weeks or months it would take for the melted unbroken glassy lump to revert to the higher melting-point is not yet known, as sufficient time had not elapsed. So far, this has been found to be 62—63°, and in one case three months had passed between the fusion of the substance and the determination of the melting-point. The method of observing the melting-point of the spangles was to place them on a thin glass microscope slide cover-glass, to float this on mercury, and to observe the melting of the spangles with the aid of a lens. At near the melting-point the temperature was only allowed to rise very slowly.

The ready discoloration when bromine water was added to the saturated aqueous solution, with the formation of an insoluble bromide, indicated unsaturation, but this was not confirmed by an alkaline solution of potassium permanganate, as the colour of very dilute solutions remained apparently unchanged for a considerable time, although eventually oxidation to dimethylprotocatechuic acid took place. There appeared to be no alteration on an attempted reduction of the substance, when it was boiled with zinc in an acetic acid solution. The formation of the bromide was also found to have been by substitution, because when bromine was added to a solution of the crystals in carbon tetrachloride, hydrobromic acid was evolved in quantity. Only one atom of bromine was introduced into the molecule by this method, and this was in the side-chain, as the bromine was readily removed by boiling alcoholic silver nitrate. The bromide was practically an amorphous body, and attempts to crystallise it were not successful, nor did it show a well-defined melting-point.

One hydroxyl group was present in the side-chain, but no aldehydic group was formed even with mild reagents, the oxidation to a carboxyl group being direct. The action of concentrated halogen acids also indicated the presence of an alcoholic OH group, and bromine was introduced into the molecule when the substance was boiled in hydrobromic acid. The molecule contains two methoxy groups, and the acid formed by oxidation was veratric acid.

Neither an aldehyde nor carbonyl group was detected, nor were indications for the presence of an ester or of a glucoside obtained.

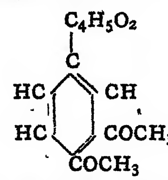
When fused with potash below 200° C., phenolic bodies were principally formed, but when the temperature was increased to about 225° the action became more energetic and the principal product was protocatechuic acid, a very small amount of a volatile acid being produced at the same time. The substance thus has a catechol nucleus.

When more material shall be obtained attempts will be made to determine accurately the arrangement of the atoms in the side-chain. The constitution of the remainder or the molecule is shown from the results.

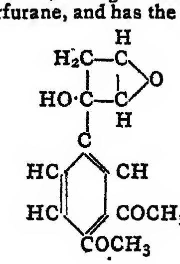
The oxidation to veratric acid, the formation of protocatechuic acid on fusion with potash, the presence of one or more asymmetric carbon atoms, together with the other reactions, suggest a structural formula for this substance in agreement with that of several bodies found in plants, all related to a dihydric phenol, the OH groups of which are in the 3 and 4 positions.

The evidence so far obtained indicates that the crystalline substance which deposits in the timber of *Gmelina Leichhardtii* is new to science, and the name Gmelinol is proposed for it.

The molecule of gmelinol is $C_{12}H_{14}O_4$ and the formula may be arranged as follows :—



The exact positions of the atoms in the side-chain have not been accurately determined, as they can be arranged, theoretically, in several ways. The one perhaps the most promising from general reactions, particularly the red and green colorations given by the vapour to pine-wood moistened with hydrochloric acid, is to consider the side-chain as consisting of furfurane. This is attached to the nucleus by the β' carbon atom, the double bond broken, the valency completed by one hydrogen attached to one β-carbon atom, and a hydroxyl group to the other. The alternative structure for furfurane with only one double linkage answers to requirements better than the usually accepted form. If this arrangement is eventually found to be the correct one, then gmelinol is dimethyoxphenyl-$\beta\beta'$-hydro-oxyfurfurane, and has the following structure :—



The positions of the nitro groups in the dinitro compound are evident.

The characteristic features of gmelinol may, for convenience, be summarised as follows:—Melting-point of crystals, 122° C. (cor.); of fused substance, 62—63°. Needle prisms or plates from hot water. Moderately soluble in boiling water, but little soluble in cold water. Almost insoluble in ether and in benzene. Insoluble in alkalis. Soluble in nitric acid with yellow colour and formation of a dinitro compound. Soluble in concentrated sulphuric acid with a deep red colour. Forms a dark brown amorphous substance when heated with hydrochloric acid. Specific rotation in chloroform $[\alpha]_D = +123.3°$. Chromic acid in acetic acid produces dimethylprotocatechuic acid (veratric acid); alkaline solution of potassium permanganate also produces veratric acid. Potash fusion at about 225° gives protocatechuic acid.

Experimental.

In one of the pieces of timber from northern New South Wales a small hollow in the wood had become filled with a solid crystalline mass, the greatest thickness of which was about one-eighth of an inch, but the usual mode of occurrence appears to be in thin veins more or less distinctly crystallised in rosettes. The substance was scraped off and boiled directly in water, filtered boiling hot, the stem of the funnel being lightly plugged with cotton-wool. As the water cooled, well-defined crystals formed, which, when of sufficient size, fell to the bottom of the vessel. This procedure was repeated three or four times, by which time the crystals had become colourless and appeared to be pure. The usual method of preparation was to saw the unsound timber into small pieces, divide along the "shakes," and trim the sides with a chisel. The shavings so obtained were then heated in alcohol to dissolve the substance, filtering the alcohol through cloth. Although it is somewhat soluble in hot alcohol, yet, if this was deficient in amount, a quantity of the substance soon separated on cooling. This separated portion was, however, identical in composition with that remaining in solution, as its identity was determined by separate purification. The alcohol was partly distilled off, and the remainder evaporated down to a small bulk which formed a crystalline mass on cooling. These impure crystals were then dissolved in boiling water, a portion at a time, filtering boiling hot, and this process repeated until the crystals were pure.

The crystals as thus obtained from water were rhombic prisms or plates, and they polarised very well in colours. They were of a glistening nature, and had altogether a brilliant appearance.

The crystals were insoluble in petroleum ether, slightly soluble in ether and in benzene, somewhat soluble in hot alcohol, but not very soluble in cold alcohol. They were exceedingly soluble in chloroform and carbon tetrachloride, but from these solvents a varnish remained at first, which slowly reverted to the crystalline form after several days.

The crystals dissolved in boiling water, but not very readily, separating out again on cooling. The pure crystals required 1470 parts of cold water at 22° C. to dissolve one part of substance, and the purest crude material in the wood was only soluble 1 part in 1315 parts of cold water at the same temperature, indicating the comparative absence of soluble impurities associated with the crystalline deposit when in the wood.

The aqueous solution of the pure crystals was quite neutral, and did not reduce Fehling's solution, either before or after boiling in acid. An ammoniacal solution of nitrate of silver was slightly reduced on long boiling. No coloration was obtained with ferric chloride, and the usual reagents gave no precipitate, except a very slight one with basic acetate of lead. The crystals were insoluble in potash and in the alkalis generally, even on boiling, except when the solution was sufficiently dilute to act like water, in which case the crystals separated unchanged on cooling.

In glacial acetic acid the crystals dissolved readily and without colour. With nitric acid they dissolved with a yellow colour forming a dinitro compound. With sulphuric acid they dissolved forming a very deep ruby or reddish brown colour, and on adding water a purple-brown precipitate separated. When heated with hydrochloric acid a dark brown amorphous substance was produced.

Analyses of the crystals gave the following results:—

0.1872 grm. gave 0.4444 grm. CO_2 and 0.1066 grm. H_2O; C = 64.74 and H = 6.327 per cent.
0.1574 grm. gave 0.3740 grm. CO_2 and 0.093 grm. H_2O; C = 64.803 and H = 6.565 per cent.
$C_{12}H_{14}O_4$ contains C = 64.865 and H = 6.307 per cent

The molecular weight was taken in Beckmann's apparatus using alcohol as the solvent.

0.4775 grm. in 16.4 grms. alcohol increased the boiling-point, 0.16°. The molecular weight calculated from this is 209. By the freezing method with acetic acid as solvent, one determination gave 228 as molecular weight, but with other trials abnormal figures were obtained; this was also the case when boiling chloroform was used as solvent.

From the results in other directions it is necessary that four atoms of oxygen at least should be present in the molecule, so that $C_{12}H_{14}O_4$ may be assumed to be correct.

Optical Rotation.—The optical rotation was taken in chloroform as this appeared to be the best solvent for the purpose.

0.3 grm. crystals in 10 cc. $CHCl_3$ rotated the ray 3.7° to the right in 100 mm. tube; the specific rotation from this $[\alpha]_D = +123.33°$.

0.6 grm. crystals in 10 cc. $CHCl_3$ gave rotation 7.4° to the right in the same tube, showing the specific rotation to be the same for both.

0.3 grm. crystals was just melted in a beaker, the glassy substance dissolved in chloroform and made up to 10 cc., the optical rotation was again +3.7°, so that no alteration was observed between the crystalline and amorphous conditions of the substance.

The molecule thus contains one or more asymmetric carbon atoms, which, from the known constitution of the remainder of the molecule, must be in the side-chain.

Dinitro Compound.—The crystals were dissolved in nitric acid, and gently heated to start the reaction. When this was completed the addition of water gave a lemon-yellow precipitate, which, when purified, was soluble in, and crystallised from, both ether and alcohol. It was readily purified from boiling water in which it readily dissolved, but separated out again in masses of yellow felted crystals on cooling. The melting-point was sharp at 128—129°, although it agglutinated some degrees below that temperature.

0.1756 of the nitro compound gave 14 cc. of nitrogen at 17° C. and 755 mm. pressure, which equals 9.14 per cent nitrogen. $C_{12}H_{12}(NO_2)_2O_4$ contains 8.98 per cent nitrogen. It is thus shown to be a dinitro compound.

Methoxy Groups.—The ready formation of insoluble halogen compounds when the crystals were boiled in a halogen acid made the results somewhat erratic. Figures more nearly correct were obtained when acetic anhydride was added, but even then the results were not too satisfactory. The greatest amount of silver iodide obtained in six determinations only represented about one and three-quarter groups of OCH_3, but this, together with the formation of veratric acid on oxidation, is sufficient confirmation for two OCH_3 groups in the molecule.

Hydroxyl Group.—A portion of the crystals was boiled with acetic anhydride and sodium acetate in the usual way. On the addition of water a crystalline substance separated, which, when purified from acetic acid melted at 110° C. Analysis gave results in conformity with one OH group. When saponified by boiling with standardised alcoholic potash the following results were obtained:—0.3684 grm,

boiled two hours had used 0·0756 grm. KOH. 0·41 grm. boiled one hour had used 0·084 grm. KOH. $C_{12}H_{13}(OCCH_3)O_4$ would require 0·0781 grm. KOH in the first instance, and 0·087 grm. KOH in the second. One hydroxyl group is thus indicated, and as this is not phenolic it must be in the side-chain.

Bromide.—The bromide was formed by the addition of bromine water in excess to the saturated aqueous solution of the pure crystals. It was light drab in colour, and was not distinctly crystalline. When well washed and purified from ether it melted at about 100°, darkening much at about 90°, but the melting-point was not sharp.

Determination of the bromine gave the following results:—0·3435 grm. gave 0·2114 grm. AgBr = 26·2 per cent bromine. 0·1554 grm. gave 0·0985 AgBr = 26·9 per cent bromine. $C_{12}H_{13}BrO_4$ contains 26·58 per cent bromine. One bromine atom had thus been introduced into the molecule. When the bromide was boiled in alcoholic silver nitrate, a precipitate quickly formed; the metallic silver was boiled out from this with dilute nitric acid, the residue washed, dissolved in ammonia, and precipitated again by nitric acid. The bromine atom was thus shown to have been introduced into the side-chain.

Oxidation.—The crystals were dissolved in glacial acetic acid and chromic acid in the same solvent slowly added until in excess. The oxidation commenced at once with the evolution of heat, the flask was then cooled under the tap. A chromium salt, which appeared to be insoluble in glacial acetic acid, continued to form until the reaction was complete. This salt was filtered off through cloth, squeezed, and the solid cake thus obtained dissolved in water, in which it was readily soluble. The solution was then acidified, extracted with ether, and after the removal of the acetic acid a solid acid remained. This was dissolved in dilute alkali, filtered, acidified, and the solution extracted with ether. The acid thus obtained was fairly soluble in boiling water but precipitated again on cooling, so that it could be easily purified. The acid sublimed unchanged. The melting point of the sublimed acid was the same as that of the acid obtained from water; this was 180° C. (cor.). It was found to melt at identically the same temperature as a sample of pure veratric acid, nor was the melting point different when equal parts of the new acid and veratric acid were mixed together. The molecular value was determined by titration and agreed very well with that of veratric acid.

When a very dilute alkaline solution of potassium permanganate was added to a large quantity of a saturated aqueous solution of the crystals the colour remained persistent for a long time; it then slowly faded with the formation of the oxide of manganese; oxidation had thus taken place. The acid formed in this way was collected, purified by sublimation, and found to melt at the same temperature and to be identical with the acid formed by oxidation with chromic acid. It was thus veratric acid.

It is apparent that oxidation of the side-chain had taken place in both instances, with the formation of dimethylprotocatechuic acid.

When oxidised with bichromate of potassium and sul phuric acid with the aid of heat, the action was too energetic, and most of the substance was destroyed by this method.

Potash Fusion.—When the crystals were heated with potash at a temperature not exceeding 200° C. for one-half hour, the colour of the melted substance had become very dark, and phenolic bodies were largely formed. The odour of creosote was most marked. The melt was dissolved in water, and the solution repeatedly agitated with ether to remove the unaltered substance. The remainder was acidified, extracted with ether, and the ether evaporated. The residue was treated with a solution of sodium carbonate, to fixed the small amount of acid formed at the same time, and this solution again extracted with ether. The phenol thus obtained had a marked creosote odour, was but little coloured, was semi-solid, and practically insoluble in water. The alcoholic solution was coloured a bluish green to dark green with ferric chloride, indicating its relation to the catechol group.

A fresh portion of material was fused with potash between 210° and 225° C. for one hour. The action was more energetic at this temperature, with frothing and evolution of hydrogen. The melt was dissolved in water, when the creosote odour was again observed. The solution was acidified, and three-fourths distilled over, and although acid, yet the amount of free acid formed was very small indeed. The remainder was agitated with ether, the ether evaporated to dryness, the crystalline residue dissolved in sodium carbonate, and agitated with ether to remove the small amount of phenol. The alkaline solution was acidified, extracted with ether, the ether evaporated, the residue dissolved in water, and decolorised by boiling with animal charcoal. The crystals finally obtained were very soluble in water, melted at 198°, and gave all the reactions for protocatechuic acid. The yield of acid formed in this way was very good.

In am indebted to my colleague, Mr. R. T. Baker, F.L.S., the Curator, for botanical information, and to Mr. Roughley for photographs.

THE SCIENTIFIC WEEK.

(*From Our Own Paris Correspondent*).

Fleas can Transmit Infectious Diseases.

The flea has already been the object not only of maledictions but also of serious allegations. Like many other insects, it is not content with victimising human beings, but it must also inoculate them with infectious germs. In a note presented to the Academy of Sciences of Paris, M. Laveran has indicated that all kinds of fleas do not offer the same dangers. The eminent hygienist has, however, signalled most particularly the flagellant flea, which secretes in its intestine a very dangerous parasite. The flagellants also are sometimes to be met with in the dog. It results, from certain experiments made at the Pasteur Institute, by MM. Laveran and Francini, that mice have been infected by injecting into their peritoneum the contents of these parasites diluted in a little physiological water. This had already been remarked in 1912 by Lafont, who had operated with a flagellum from the digestive tube of a bug. M. Laveran has not stated whether men or dogs could be infected by the contact of these fleas, but the effect produced upon the mouse is sufficient to make us uneasy. So let us continue to fight against this troublesome insect and to destroy it everywhere by all the means in our power.

The Consumption of Paper.

Paper may be divided into three great classes—fine, high-class, ordinary paper for current uses, and paper for folding. It is certain that the consumption of the higher classes of paper is increasing, but very slowly, and this industry will always find sufficient raw material for its requirements, more especially as the scale of its prices is very elastic. The same cannot be said for the second class, that of paper for ordinary use; that is to say, paper intended for daily uses, such as newspaper editions, prospectuses, and generally speaking for all printed and written matter. It is this consumption that is continually increasing, and whose needs and demands of paper are ever becoming more and more imperious. It is in order to fulfil these requirements, considerably increased by the use of rotary printing machines, with a large output, that the stationery industry has also been obliged to create paper machines of great width and great speed, which can turn out as much as forty or fifty tons of paper in twenty-four hours; it is also for this kind of paper the forests are pillaged. When there is no longer a sufficient quantity of wood to be had, with what will these paper-mills be fed? At that moment the only wood remaining

will be that obtainable from the annual growth of forests reserved and arranged for periodical cuttings, and the stationery industry will have to share them with other industries. M. Henry Montessus de Ballore, in his interesting technical work, tries to solve the question concerning the future resources in raw material of paper manufacture. He has drawn up a list of those materials of which the cellulose could be used for the manufacture of paper.

Besides wood, to feed the paper-mills in the future, we have: Plants that grow spontaneously, bamboo, papyrus, alfa; the refuse of various industries, rags, cables, cords, strings; the refuse of spinning-mills, cotton, linen, hemp, jute, phormium; the refuse of agriculture, wheat and rye straw, oat and rice straw, the stalks of Indian-corn, and the refuse of the sugar-cane.

M. de Montessus de Ballore has specially studied each of these matters, their treatment, their yield, and the rise of the pastes obtained; lastly, he has noted some plants that, at least for the present, appear to have only a very restricted future in the paper industry.

VARIABILITY OF NEBULÆ.

The question of the variability of the brillancy is now discussed after having been considered as certain. Astronomers are to-day apt to look upon it as doubtful, and that on account of the difficulty of conceiving the mechanism of such a variation, as much in the case of resolvable nebulæ or masses of stars as in the case of non-resolvable or purely gaseous neublæ. A nebula discovered by Hind in 1845, in the constellation of the Eagle, was considered as variable; quite recently, M. Borelly announced that at present it appears to be attaining a maximum state of brilliancy. M. Bigourdan shows that former observations do not confirm the variability. He insists on the interest of the fact noticed by M. Borelly, and on the importance just at present of the observation of the Hind Nebula, as this is just now very distinctly visible in instruments of average opening.

THE AERIAL GULF STREAM.

The Gulf Stream, when it leaves the Gulf of Mexico, enters the Atlantic with a speed of 8 kilometres an hour. It is 60 kilometres wide and 400 metres deep, and daily transports about 40 millions of milliards of calories. This enormous quantity of heat, of which it is almost impossible to obtain an exact idea, plays a fundamental rôle in the general climatology of the earth. Strangely enough it is this stream of hot water, exercising its temperate action on the coasts it waters, which is the direct cause of the existence of deserts. And this is how. Water is one of the bodies in which heat is the most easily preserved, and consequently the Gulf Stream even in high latitudes still keeps an enormous quantity of heat. The masses of air that rest on these hot waters are kept at a temperature higher than the surrounding temperature and form a veritable aërial gulf stream superposed over the marine current. But the aërial current is not like the marine one arrested by the mass of the continents. It continues its route above Europe, abandoning, in the form of rain, the enormous masses of water it contains; it is these abundant precipitations which feed the numerous lakes of Sweden, Finland, and Northern Russia. But, on account of the rotation of the earth, the aërial current turns first to the east, then inclines towards the south. It thus constitutes masses of dry cold air which give to the plains of Russia their principal meteorological character. As it draws nearer to the Equator the current is again warmed, but remains at the same time dry and without vapour; its direction is then north-east, and it is in the state of a drying wind that it blows over the regions it crosses. It is the origin of the band of deserts of Turkestan, Arabia, Sahara, which are to be found on its return route. After having left the Continent, the aërial current, thanks to the trade-winds, links itself on again to its starting point, the Gulf Stream, thus looping its circuit after having, like everything else, done much good and much evil.

ELECTROMAGNETIC WAVES.

The laws governing the propagation of radio-telegraphic signals in the atmosphere during the day and during the night are still but imperfectly known, and the development of aëronautics has enabled us to gather some interesting information on this subject. The signals grow weaker as the distance increases, but one of the points to be examined is to know how the height above the ground influences this problem; in other words, are the signals affected by a weaker density, a lower temperature, and by the intense ionisation of the high regions of the atmosphere. M. G. Lutz has given several results obtained in utilising a balloon of 1680 cubic metres, with a circumference of 45 metres. The autenna was formed by a metallic wire of 100 metres long hanging under the basket. During the experiments made in the night, the balloon covered a distance of 120 kilometres at an average altitude of 1277 metres. It was found that the intensity of the signals received decreased when the distance increased, but that this weakening is not proportional to the square of the distance; it varies as the power 1·96 of the distance and when far from the starting station, as the power 0·88. At an equal distance it is remarked also that the signal is so much the weaker as the balloon is higher. To be more precise on this point, a second ascension was made, the balloon then rising to a height of 6500 metres. At this height, the intensity of the signals equalled what they would have had on the earth at the same distance from the station. These results are worth being confirmed and completed, for the question is still but very incompletely known, and up till now the experiments have been insufficient.

NOTICES OF BOOKS.

Studies in Valency. By F. H. LORING. London: Simpkin, Marshall, Hamilton, Kent, and Co., Ltd.

IN this little book certain relations between the combining powers of the elements are shortly discussed, and some new lines of experimental work are suggested. The valencies of some of the elements which are specially interesting, such as vanadium and bismuth, are treated in detail, and a chapter is devoted to the consideration of electricity as a conditioning agent in chemical changes, and another to modern theories of atomic structure based upon experiments in molecular physics. The author has evidently carefully studied the literature of theories of valency, and he shows much skill in stating briefly the gist of an argument and ingenuity in pointing out the directions in which fruitful research may possibly be undertaken.

Laboratory Methods in Agricultural Bacteriology. By F. LÖHNIS, Ph.D. Translated by WILLIAM STEVENSON, B.Sc., N.D.A., N.D.D., and J. HUNTER SMITH, B.Sc., N.D.A., N.D.D. London: Charles Griffin and Co., Ltd. 1913.

THE need of such a work as this in the English language has long been felt by agricultural teachers and students, who have found considerable difficulty in devising and satisfactorily carrying out the practical work in bacteriology which is an essential complement of the study of the theory of the subject. The technique of bacteriology is first described, and clear directions are given for preparing culture media and isolating and examining bacteria. The use of only comparatively simple apparatus is recommended, and sources of error to be avoided, and the precaution which must be adopted to ensure successful work are repeated pointed out and emphasised. The application of general methods to dairy, manure, and soil bacteriology is then described in detail. Tables are given for the identification of bacteria, and the question of laboratory equipment is shortly discussed. The book is sure to

receive a hearty welcome from the many agriculturists who, while unable to study bacteriology in Prof. Löhnis's own laboratory at Leipzig, are fully aware of the importance of the subject as applied to agricultural problems and of the great value of his work in it.

Simplex Atomic Models. Designed by E. G. Lester, B.Sc. Birmingham: Philip Harris and Co., Ltd.

Teachers of chemistry will undoubtedly find that these models greatly diminish the difficulties of theoretical chemistry for the young beginner. They have the advantages of being simple and cheap, and by means of them the boys can themselves build up structural formulæ, work out equations, and illustrate the laws of chemical combination, while they should be simultaneously acquiring clear ideas of valencies, variable valencies, &c. The boxes of models contain a little stand, a number of wire links, and detachable cardboard discs (pink in the case of nonmetals, white for metals) with the symbol, valency, and atomic weight of the elements printed on them. Some blank discs are also included for use as compound radicles. With the necessary links and discs the pupil can build up such formulæ as $\begin{matrix}Na-O\\Na-O\end{matrix}\!>S\!\begin{matrix}=O\\=O\end{matrix}$, &c., and it will undoubtedly mean much more to him than the same formula written on a blackboard. It may of course be objected that he will form some very concrete and erroneous conceptions as to valencies, but that is perhaps unavoidable, at any rate in an elementary exposition of the subject, and in the hands of a good teacher the models should be a valuable educational aid. By bending the wire links the models can be used to illustrate the arrangement in space of carbon compounds.

Metropolitan Water Board. Ninth Research Report. By Dr. A. C. Houston.

The ninth research report of the Metropolitan Water Board contains accounts, with tables and diagrams, of the search for pathogenic microbes in raw river water and for the typhoid bacillus in sewage. The results of the investigations show that the purification processes practised by the Board amply safeguard the health of the metropolis. The consideration of the question, "Where is the typhoid bacillus?" appears to lead to the conclusion that its home is not so much in impure water, nor even in crude sewage, as in the "factories" of disease, as exemplified by the "carrier" case.

OBITUARY.

DR. LOUIS MERCK.

Dr. Louis Merck, the head of the famous firm of E. Merck, of Darmstadt, died on September 15th after a short illness. He had been connected with the firm for over thirty years, and for twenty-five years had been its senior partner. The growth and wonderful success of the house were largely due to his foresight, energy, and enterprise, and his loss will be very severely felt.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Bulletin de la Société Chimique de France.
Vol. xiii.-xiv., No. 13, 1913.

Cryoscopy in Fused Hydrated Salts.—Ch. Lenhardt and A. Boutaric.—The melting-point of a hydrated salt is lowered by the presence of a dissolved substance, and it is the same with the equilibrium temperature which is established between two solid hydrates and an excess of solution. The authors have investigated whether the cryoscopic formula of van't Hoff, $K = 0{\cdot}01985\ T^2/L$, is applicable to these phenomena, and, using sodium hyposulphite with five molecules of water and sodium sulphate with $10H_2O$, they have found that the formula holds good.

New Physico-chemical Volumetric Method.—René Dubrisay.—The author has devised an acidimetric method, based upon capilliary phenomena, which is both simple and accurate. He makes use of the fact that when an oil is shaken with water containing alkali, the drops formed remain in suspension and an emulsion is obtained. When the water is neutral or acid no emulsion is formed, but after a few moments the liquid divides into two layers. According to Tate's law, the weight of a drop of liquid which detaches itself from the extremity of a pipette is proportional to the superficial tension of the liquid. Thus if N is the number of drops corresponding to the flow of an invariable volume $N = A/\delta$, where δ is the superficial tension and A is a constant. If the drops are counted when oil of vaseline flows into a solution of acid to which increasing quantities of alkali are added, and the results are expressed graphically, it will be seen that the curve has an abrupt turning point at the point of neutralisation.

Catalytic Preparation of Ketones.—A. Mailhe.—The author has repeated his experiments on the catalytic preparation of ketones, using zinc or cadmium oxides as catalysts, since his results were questioned by M. Senderens. He finds that both oxides, either alone or mixed with the metals, are good catalysts, except in the case of isobutyric and isovaleric acids, which give either very poor yields of ketone or none at all. Calcium carbonate is also a good catalyst for acids.

Nitro Derivatives of *p*-Phenetidine. — Frédéric Reverdin and Ludwik Fürstenberg.—Of the nine possible nitro derivatives of *p*-phenetidine three only have hitherto been described. By the nitration of the acyl derivatives of the base the authors have now succeeded in preparing three new compounds, viz., the 3.5-dinitro derivative, the 2.6-dinitro derivative, and the 2.3.5-trinitro derivative.

Atti della Reale Accademia dei Lincei.
Vol. xxii. [i.], No. 10, 1913.

Compounds of Monovalent Nickel.—J. Bellucci and R. Corelli.—Red solutions of nickel cyanide evolve hydrogen at the ordinary temperature, and measurements of the amount evolved show that it corresponds with that which would be generated in the change from NiX to NiX_2. Iodometric determinations also show that the red solution also contains a compound of monovalent nickel.

Action of Hydroxylamine on Ketones of the Type R.CH:CH.CH:CH.COR.—R. Ciusa and G. B. Bernardis.—When hydroxylamine hydrochloride acts on the ethyl ether of cinnamilidenepyruvic acid a substance of formula $C_{26}H_{34}O_9N_4$, fusing at 213°, is obtained. It contains a molecule of alcohol of crystallisation, and is formed by the union of two molecules of the hydroxylamine oxime of cinnamilidenepyruvic acid, combined in such a way as to mutually saturate the double bonds. The substance $C_{24}H_{28}O_8N_4{\cdot}C_2H_5OH$ immediately gives an insoluble sodium salt when treated with sodium carbonate. It is decomposed by boiling with dilute sulphuric acid. In the original reaction a small amount of a substance of formula $C_{26}H_{31}O_8N_4NO$ is also obtained.

NOTES AND QUERIES.

Aluminium Sulphate.—A correspondent asks for a reference to a process for manufacturing aluminium sulphate from bauxite by the use of gypsum instead of sulphuric acid.

MEETINGS FOR THE WEEK.

Friday, 10th.—Biochemical Society, 8.30. (In the Department of Chemical Pathology, St. Thomas's Hospital, London).
— Alchemical Society, 8.15. (At International Club, Regent Street). Address by the Hon. President, Prof. John Ferguson, M.A., LL.D., &c.

THE CHEMICAL NEWS.

Vol. CVIII., No. 2811.

THE CHEMISTRY OF THE RADIO-ELEMENTS.*

By ALEXANDER FLECK, B.Sc.,
Assistant in the Department of Physical Chemistry, Glasgow University.

The fact that it is impossible to separate some of the radio-elements from some one or other common element is not a new one. Welsbach has attempted to separate thorium and ionium, Herschfinkel and Hevesy and Paneth have tried radio-lead (radium D) and lead, Hahn and Boltwood radio-thorium and thorium, Hahn thorium X and mesothorium-1, Marckwald and Soddy mesothorium-1 and radium, and Marckwald and Keetman uranium X and thorium, but in none of these cases has it been found possible to separate one element from the other once the two had been mixed together in solution. It was to be expected, therefore, that similar cases would exist among the shorter-lived radio-elements, and it is proposed to describe briefly the experimental methods that have been employed in examining the chemical nature of these substances.

In the first place it has to be noticed that, as a rule, we have to find the chemical nature of unweighable quantities of material. To give two examples, the amount of uranium X in equilibrium with 50 grms. of uranyl nitrate is as much as can be conveniently worked with, and this quantity weighs only 10^{-9} of a grm. In the case of radium A this quantity is far too large and 10^{-12} grm. is ample for most purposes. It is therefore evident that the chemical nature of these bodies must be worked out in the presence of what is really an impurity of many thousand times the actual weight of the radio-element present.

The first step in the determination of the chemical nature consists in finding what known element our radio-element most resembles. This is done by making a mixture of three elements in solution—two ordinary elements which can be easily isolated and the radio-element. The two elements are then separated and each portion tested under the electroscope, when it will usually be found that the radio-element is definitely associated with one or other portion. For instance, if we have a solution of thorium B, iron, and calcium, and ammonia is added to the solution the thorium B will be found to be precipitated with the iron. By a number of such experiments it can be shown that thorium B must belong to the first, second, or third group of metals, and by a similar process, say, with a mixture of copper and iron, the third group is eliminated and it must belong to the first or second. Sometimes it happens that the radio-element does not identify itself solely with either of the common elements, as when we separate a mixture of iron and uranium containing mesothorium-2, but divides itself between the two, but as a rule by proceeding in the manner indicated it is possible to say that the radio-element resembles in a general way one of the common elements, as, for example, radium E and bismuth. The second step is to find whether this resemblance amounts to an identity or is merely a similarity, as polonium and bismuth. It is well known that if a mixture of polonium and bismuth is heated strongly the first fractions to volatilise are richer in polonium. The method then consists in making a mixture of the radio-element and the common element, to which the former bears most resemblance, and submitting the mixture to some fractional treatment, the exact nature of which is, of course, dictated by the nature of the common element. In the case of thorium B, which was known to resemble lead, a quantity of lead chloride which had been crystallised from a solution containing thorium B was volatilised in a vacuum, and thus divided into fractions in the order of their volatilities. Successive measurements of the activity of these fractions were taken over a period of twenty-four hours, and thus the relative quantities of thorium B in each one obtained. The quantity of lead in each was then estimated by the usual gravimetric process, and in this way the activity per grm. of lead in each fraction was obtained, and it was found that for any one experiment this quantity was constant within the limits of experimental error. In all such cases β-rays were used to determine the quantity of the radio-element present, and the common element was there in such small quantities, usually spread out in a thin layer, that the absorption of the β-rays by it was negligible. By such methods the following results were proved:—

1. Uranium X and radio-actinium are chemically identical with thorium.
2. Radium C, thorium C, actinium C, and radium E are chemically identical with bismuth.
3. Radium B, thorium B, and actinium B are chemically identical with lead.
4. Thorium D and actinium D are chemically identical with thallium.

Mesothorium-2 was the first case that was met with in which it was impossible to find a resemblance to a common element, and when its analogy with actinium was suspected special methods had to be devised for the measurement of the latter element, since it itself is rayless and since it has not been possible to obtain it free from other matter. Mesothorium-2 was separated from a strong mesothorium preparation in solution by the precipitation of zirconium hydroxide, and this small quantity of material added to an acid solution of actinium contained in lanthanum. The actinium had been freed a very short time previously from radioactinium and actinium X, and was therefore rayless. The solution thus obtained contained mesothorium 2, actinium, zirconium, and lanthanum, of which only the first gave β-rays. The solution was then fractionated, and during the two following days β-rays were measured, and thus a measure of the quantity of mesothorium-2 in each fraction was obtained. In the course of two to three months the actinium had grown radioactinium and actinium X, which in turn had grown actinium D, a β-ray-giving body, and the measure of the activity then was a measure of the amount of actinium present. In this way it was found that the ratio of mesothorium-2 to actinium was constant.

The second case when no resemblance with a common element was found was radium A and polonium. In this case to measure radium A and polonium when both were present, use was made of the difference of the ranges of the α-particles coming from these substances. To obtain quantitative information regarding the identity of the two, the only way that was found possible was to deposit both simultaneously on gold, platinum, silver, or copper plates. In every experiment it was found that the ratio of polonium on any two plates was approximately equal to the ratio of radium A. Absolutely exact experiments were not possible, since the radium active deposit had to be dissolved from a magnesium plate, the solution thus obtained added to the polonium solution, the deposit obtained on the plates, which had then to be washed and dried, and sufficient readings for each plate had to be taken, all within seven or eight minutes from the instant of the withdrawal of the active deposit from the emanation.

The last part of the work concerns the chemical nature of uranium X_2, which has recently been discovered by Fajans and Göhring, and which has a period of half value of 1·1 minutes. This body is not precipitated as sulphate, but otherwise is very easily precipitated, and this is in complete agreement with what one might predict from its position in the V. A family of the Periodic Table. It

* A contribution to the discussion on "The Radio-elements and the Periodic Law," in Section B, British Association, Birmingham, 1913.

would be expected also that this substance should be volatile in the presence of hydrofluoric acid, since tantalum fluoride—a volatile body—is more volatile than the corresponding salt of niobium. However, it was found to be absolutely non-volatile, but it must be remembered, to repeat an observation made in *Nature* some time ago in a different connection, that whereas Mendeleeff made his predictions by interpolation. in this case it was necessary to extrapolate, and thus some uncertainty is introduced. The general similarity of Uranium X_2 to tantalum is shown by Hahn and Meitner's experiment, that if a solution of uranium X is filtered through a layer of tantalum pentoxide, the uranium X_2 alone is adsorbed.

One point that may be referred to is the relation between the radio-elements and the rare earths. The question may be asked: Is it not possible that the so-called non-separable elements, *e.g*, thorium, radiothorium, ionium, uranium X, and radioactinium, stand to one another in the relation of a rare earth group, and if that was so could we detect the fact? The electroscope gives us a means of detecting minute variations in the concentration of the radio-element, and when no alteration in concentration was found, after ten successive precipitations within a limit of experimental error of about 4 per cent, the experimental evidence shows that these radio-elements are not analogous to the rare earths. By rearranging the Periodic Table, as has been done by Werner, it has been possible to find a place for all the rare elements, but in no system that has been put forward yet would it be possible to get the thirty-eight radio-elements into the last series. No provision is made in the ordinary Periodic Table for bodies having the same atomic weight but different properties, such as we have in the radio-elements, *e.g.*, mesothorium-2 and radiothorium. These bodies have the same atomic weight, but can be separated from one another as easily as iron from calcium. Finally, our chief evidence for the existence of a number of rare earths is differences in their spectra, while the spectra of non-separable radio-elements are believed to be identical, although it must be remembered that there is only the one case of thorium and ionium where this has been proved. These considerations show that we are not dealing with substances similar to rare earths, and that there is no analogy between the two cases.

It is to be noticed that in all cases in which the non-separable elements are common elements these latter all have atomic weights of over 200, and occupy one or other of the last twelve places in the Periodic Table.

In conclusion, in addition to the results already given, we have the following, obtained by special methods:—

5. Mesothorium-2 is chemically identical with actinium.
6. Radium A is chemically identical with polonium.
7. Uranium X_2 has a chemical nature peculiar to itself.

Although these results are often put in an apparently negative form—that thorium B is non-separable from lead, &c.—this is not a negative statement, but is merely a convenient way of stating that these radio-elements have characteristic chemical properties and can be separated from any of the other eighty or so elements.

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THE ACTION OF AN ALKALINE NATURAL WATER ON LEAD.*

By J. F. LIVERSEEGE and A. W. KNAPP.

The water supply of Birmingham is gathered chiefly in Wales. The water is slightly alkaline: it does not appreciably *dissolve* lead (absence of "plumbosolvency"), but unless treated it corrodes or "*erodes*" bright sheet lead. To prevent any danger from this action, a small proportion of powdered chalk is added to the water in Wales. This treated water flows to Birmingham through an aqueduct seventy-three miles long.

Lead Pipes.—For these experiments a series of lead pipes was connected with the supply and analyses of the water made over a period of five years. Hundreds of samples were also taken from consumers' pipes and from lengths of lead pipes closed with corks. For short periods the total lead dissolved from the pipes increased with time, but different lengths of the same pipe showed considerable variation. As a rule a pipe becomes with age less sensitive to the action of the water, but the rate of this change varies greatly with different pipes. Treatment of new pipes with a dilute solution of potassium permanganate gave them a considerable power of resistance to the action of the water.

Sheet Lead.—Many experiments were made on the sheet lead "erosion" test, and for practical purposes a duration of one day is preferred to the seven or fourteen days suggested by Dr. Houston. We find that erosion is due to the action of oxygen in the presence of water. The amount of lead eroded is affected by the distance from the lead to the water surface, is generally proportional to the area of the surface of the lead exposed, and does not depend on the volume of the water.

With untreated water carbon dioxide up to one per cent by volume produced little effect on the amount of erosion; when two or more per cent of carbon dioxide is present erosion no longer occurs, for the liquid remains clear, but lead is dissolved, in amount much less than that removed by erosion. Given sufficient oxygen, the alkalinity of the water is the principal factor determining the amount of erosion. The use of (*a*) *lime* to prevent erosion was not found satisfactory, the presence of three to nine parts per 100,000 of water reduced the erosion, but smaller or larger quantities were of little, if any, use. Four parts per 100,000 of (*b*) *calcium carbonate* gave protection, and as little as two parts per 100,000 of (*c*) *calcium bicarbonate* were sufficient to practically prevent erosion. Filtration through sand had little effect on the action of the water on lead. No evidence was found of a seasonal variation in the action of the water on lead, though the colour and amount of organic matter varied considerably.

* Read before the British Association (Section B), Birmingham Meeting, 1913.

DIRECT DETERMINATION OF THE STEATITE OR TALC-FACING ON RICE.

By E. W. T. JONES, F.I.C.

The following is a simple and expeditious way of doing this, and is independent of any variation in the natural ash of rice:—

Put 5 grms. of the rice into a 150 cc. squat beaker, pour on to it, say, 20 cc. of ether, and agitate for a few minutes; pour this off into an 80 or 100 cc. beaker containing a cc. or so of water, and evaporate the ether off on the top of the water-oven. Allow the ether to evaporate from the rice, then add to it about 15 cc. of cold distilled water, and agitate; pour off into the other beaker, and repeat four or five times till the water comes away almost clear; allow these washings to stand all night, then the nearly clear supernatant liquid can be poured off, leaving the steatite associated with a little fine rice behind; transfer this by means of a wash-bottle (I use methylated spirit to facilitate evaporation) to a weighed platinum dish, evaporate to dryness, ignite, and weigh; this gives the amount of steatite or talc-facing.

The first treatment with ether removes any oil which may tend to retain the facing, and the subsequent water dissolves the glucose fixing the same.

Wolverhampton, September 16, 1913

A NEW METHOD FOR THE DETERMINATION OF THE MOLECULAR WEIGHT OF STARCH.

By CECIL L. HORTON.

THE general formula for starch is given as $(C_6H_{10}O_5)_n$, but if we assume the compound to be a chain of dextrose molecules, built up by condensation with the elimination of water, we arrive at the formula $\{(C_6H_{12}O_6)_n-(n-1)(H_2O)\}$ ("Hollemann's Organic Chemistry"). If n is large the difference in the molecular weights obtained is very small; *i.e.*, if $n=41$.

$$(C_6H_{10}O_5)_{41} = 6642,$$
$$\{(C_6H_{12}O_6)_{41}-40(H_2O)\} = 6660,$$

and difference $= \frac{1}{4}$ per cent.

If therefore the hydrolysis starch $\rightarrow$ dextrose can be completely carried out without the production of other substances, 1 molecule of starch will create n molecules of dextrose with the absorption of $(n-1)$ molecules of water. The molecular weight of starch becomes—

$$[(180n)-(n-1)18] = 18(9n+1),$$

that of sugar being 180 and water 18.

If therefore W grms. of starch give rise to W_1 grms. of dextrose, then—

$$W : 18(9n+1) = W_1 : n180.$$
$$\therefore Wn\ 180 = 18W_1(9n+1).$$
$$\therefore n(10W-9W_1) = +W_1.$$
$$\therefore n = \frac{W_1}{10W-9W_1}.$$

Therefore by determining the weight of sugar obtained from a given weight of starch the value of n can be found. The number is of course a whole number, and by substitution in the formula $[M]=18(9n+1)$, the molecular weight can be found.

The writer some months ago endeavoured to obtain the value of n, but was unable to discover a suitable catalyst, the ordinary alkali and acid obtainable causing the formation of a brown humus in sufficient quantity to render the observations worthless. This question is still under consideration.

THE ESTIMATION OF CHLORINE IN RAG FLOCK.

By ALBERT E. PARKES, F.I.C.

THE estimation of chlorine in rag flock is now an undertaking which many analysts are called upon to perform, and methods have already been recommended by Richardson and Jaffé (*Journ. Soc. Chem. Ind.*, 1913, p. 402), and Black (*Analyst*, 1913, p. 409).

Since the Rag Flock Act came into force in July, 1912, the writer has examined a large number of samples from various sources, and at the outset devoted some time to devising a suitable process for the chlorine estimation. It was very early found that the gravimetric method applied to the aqueous extract was unreliable owing to the precipitation of other substances with the silver chloride, and the direct volumetric method could only be used when the solution was colourless. As most flocks contain soluble dyes this occurs but seldom. Finally it was found that the best results were obtained by evaporating the aqueous extract to dryness, heating to destroy organic matter, and titrating the chlorine with standard silver nitrate solution.

The complete method now adopted is as follows:—

Fifty grms. of the well-mixed sample is weighed out, placed in a large beaker with about 500 cc. of distilled water, and allowed to digest at laboratory temperature for three to four hours. It is then thrown on to a Buchner funnel in which a circular piece of fine metal gauze has been fitted. By means of the filter-pump the flock is drained, pressed dry by hand, and washed on the funnel with successive quantities of 100 cc. of water, draining and pressing between each washing, until 1000 cc. of extract has been obtained. This is finally passed through a dry filter to free it from flocculent matter.

For the estimation, quantities of 100 cc. each of this solution, representing 5 grms. of flock, are transferred to white porcelain dishes and evaporated to dryness. The dry extract is heated sufficiently to just char the organic matter, cooled, a little water added and a few drops of potassium chromate solution, and the chlorine titrated with silver nitrate solution of the same strength as used in water analysis (1 cc. = 0·001 Cl). The final solution need not be filtered as the charred matter does not interfere with the end-point of the reaction. A minute quantity of pure lime may be added to the extract before evaporation to prevent loss of chlorine during the subsequent heating, but this is unnecessary if the heating is stopped short of actual ignition.

This method has been found to give accurate results when known quantities of sodium chloride have been added, and concordant results in duplicates.

In the case of unwashed flocks made from rags and old clothes it is advisable to add to the first water some suitable germicide, such as pure phenol.

Stepney, E.

THE CHEMICAL EFFECTS OF POLARISED LIGHT.

By E. G. BRYANT, B.A., B.Sc.

IN many parts of the world, more especially in tropical regions, there is a widespread belief in the deleterious effects of moonlight on fish, and to a lesser degree on meat intended for food. This belief is by no means confined to sailors, fishermen, and other superstitious or ignorant persons. Many doctors are convinced of its truth—it has been officially given as the cause of death in at least one South African inquest; I have received some most trustworthy statements of the ill-effects produced in persons who had partaken of fish that had been so exposed. There are also closely allied beliefs as to the danger of sleeping with the tropical moon shining full on the face, the effects of moonlight on seeds, on growing plants, and the rising of the sap in wood.

It seemed to me that a possible explanation of these phenomena, supposing them to be true, might lie in the well-known fact that the light of the moon, being reflected light, is more or less polarised. I examined all the authorities at hand, but could find no reference to any work carried out on polarised light with reference to its chemical effects.

I therefore made an endeavour to test for any such effects, and this short note embodies the results I have been able to obtain. For one or two experiments I had the use of a 200 candle-power Osram lamp, but the others received only light from a 32 candle-power carbon-filament lamp. The light was polarised by means of a pile of seven sheets of plate-glass, backed with a silver mirror and placed at the correct angle. I hope to be able to continue the work with the larger lamp, as it is evident that no decisive results can be obtained without a fairly powerful beam of light.

The most marked results were obtained from fish. If two slices, cut from the same fish, were hung, one in the direct light, the other in the polarised beam, the latter invariably began to decompose before the former, though the temperature of the polarised beam was several degrees lower than the direct light. These experiments were carried out with the large lamp. Tests were arranged with the small lamp on meat, jam, cane-sugar solution

and several kinds of seeds. The sugar showed absolutely no change; of the others, none could be called decisive, but whenever any difference was observable it was always in favour of the polarised light.

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THE ACTION OF FINELY-DIVIDED NICKEL ON NITRIC OXIDE.

By R. S. FELGATE.

From thermodynamic considerations it might be expected that nitric oxide would be decomposed at ordinary temperatures when brought into contact with a suitable catalyst.

It is well known that finely-divided nickel when heated brings about the decomposition of the gas, and it has been found that cokernut charcoal cooled to the temperature of liquid air produces the same effect, yielding as final products carbon dioxide and nitrogen (Gray, "Ueber das Atomgewicht des Stickstoffs," Inaugural Dis., 1907).

It has now been found that the gas can be catalytically decomposed by finely-divided nickel suspended in hot water, the products being nitrogen and nickel oxide.

In a specially constructed glass apparatus pure nitric oxide, obtained by the fractionation of the liquefied gas and free from higher oxides, was caused to circulate through hot water containing in suspension finely-divided nickel, prepared by the reduction of the dry precipitated hydroxide in an atmosphere of hydrogen. The nickel was rapidly converted into the oxide, and the circulating gas on analysis was found to contain 20 per cent of nitrogen. After the experiment the filtrate from the suspended nickel was found to contain traces of ammonia (the amount found was no more than could correspond to the hydrogen occluded on the nickel), but since no appreciable amount of nickel was present in it and since the gas after the experiment contained no hydrogen, the possibility of the action from the presence of higher oxides is excluded. A similar experiment with colloidal nickel prepared from nickel electrodes by Bredig's method gave no result, but a third experiment with another sample of reduced nickel, prepared as described, confirmed the first result.

The action appears to depend upon the state of aggregation and method of preparation of the nickel catalyst, and further investigation of this point is proposed.

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THE EFFECTS OF SULPHATES ON THE DETERMINATION OF NITRATES.

By W. P. KELLEY.

Introduction.

As is well known, the determination of nitrates in the sanitary analysis of water is generally made with the aid of the phenoldisulphonic acid reagent. During recent years this reagent has found extensive application in soil investigation, particularly in studies on nitrification. The chemistry of the reactions involved in this determination has been extensively studied, and, as shown by Chamot and Pratt (*Journ. Am. Chem. Soc.*, xxi., 922; xxxii., 630; xxxiii., 366), the yellow colour that is produced depends upon the formation of the tri-salt of the phenoldisulphonic acid. It is not the purpose of this paper, however, to discuss the chemistry of this reaction, but rather to present some data bearing upon the effects of sulphates on the nitrate determination.

Natural waters, as well as the solutions obtained from soils, frequently contain various salts. Among these are the chlorides, carbonates, and sulphates. The effects of chlorides and carbonates on the determination of nitrates have been studied in detail, especially the former; but the fact that the phenoldisulphonic reagent contains free sulphuric acid, which upon neutralisation gives rise to sulphates, has caused chemists to neglect to study the effect of sulphates.

Recently, Lipman and Sharp (*Univ. Cal. Pub. Agr. Sci.*, i., No. 2, pp. 21—37) published some investigations on this subject in which chlorides, carbonates, and sulphates were studied. They found, in common with previous studies, that chlorides caused an apparent loss of nitrates, but, contrary to previous observations, carbonates have no effect. They further found that considerable loss of nitrate took place upon evaporating a nitrate solution containing sodium sulphate. The addition of dry sodium sulphate to the dry nitrate residue, however, occasioned no loss of nitrate. From these observations the claim is made that sulphates cause a loss of nitrate in this determination, not by interfering with the phenoldisulphonic acid reaction, but by the expulsion of nitric acid during the time of evaporation on the water-bath. Hence they conclude that nitrate determinations in solutions containing sulphate must be made by the use of other methods.

As above stated, soluble sulphates are frequently present in soils. In addition it is a common practice to employ a solution of alum as a coagulating agent in order to secure clear soil solutions. While it is true the use of alum as a coagulating agent may well be objected to for other reasons, as pointed out by Lipman and Sharp, the suggestion that sulphates in general cause a loss of nitrate during the time of evaporation merits further study. The more especially is it important that this subject be investigated, since in the numerous nitrification studies now being carried on in many parts of the world, ammonium sulphate is often used as a source of nitrogen, and therefore soluble sulphate is bound to occur in the water extracts in which the nitrate determinations are usually made.

For some time the writer, at the suggestion of Mr. S. S. Peck, of the Hawaiian Sugar Planters' Experiment Station, has made use of calcium sulphate as a coagulating agent in the determination of nitrates in Hawaiian soils. This material has proven to be a most efficient coagulating agent with the abnormal soils of the Islands, often being found to be far more effective than calcium oxide or carbonate. In fact, the last named compounds cause a deflocculation in some of the heavy upland soils, while calcium sulphate brings about rapid coalescence of the finely divided particles, thus effectively aiding in securing a clear solution. On account of the extensive use that has been made of calcium sulphate in this laboratory it became necessary to test the effect of this compound on the nitrate determination. The results proved to be so out of harmony with the conclusions reached by Lipman and Sharp that a study of some of the more common sulphates was also undertaken.

Experimental.

The nitrate solution used in this work was prepared by dissolving in distilled water potassium nitrate at the rate of 250 parts of nitrogen per million, and portions of the solution containing the amounts of nitrogen shown in the subjoined tables were taken in all of the determinations reported in this paper. The sulphates were employed in solution prepared by dissolving 1 grm. in 1 litre of distilled water, and varying amounts were added to the nitrate solution, as shown in the tables. After evaporating on a water-bath, and cooling, the residues were treated with 2 cc. of the freshly prepared phenoldisulphonic acid reagent, allowed to stand five minutes, diluted to about 30 cc., and the colour developed by carefully adding strong ammonia until alkalinity was produced and a permanent colour obtained. After diluting to 250 cc., aliquot

portions were then used for making comparisons in a colorimeter with a standard nitrate solution prepared in the same way. All determinations were made in duplicate. The results follow:—

Effects of Sulphates on the Determination of Nitrates.

(0·275 mgrm. Nitrate Nitrogen Used in each Determination).

Sulphate added.	Na_2SO_4. Nitrate N found.	K_2SO_4. Nitrate N found.	$MgSO_4$. Nitrate N found.	$(NH_4)_2SO_4$. Nitrate N found.	$CaSO_4$. Nitrate N found.
Mgrm.	Mgrm.	Mgrm.	Mgrm.	Mgrm.	Mgrm.
None	0·275	0·275	0·275	0·275	0·275
1·00	0·275	0·280	0·272	0·237	0·270
5·00	0·265	0·270	0·277	0·203	0·270
10·00	0·225	0·210	0·270	0·235	0·273
20·00	0·180	0·265	0·275	0·225	0·273
40·00	0·140	0·260	0·277	0·225	0·280

It will be seen from the above data that when any considerable amounts of sodium, potassium, or ammonium sulphate were added considerable loss of nitrate took place, whereas neither calcium nor magnesium sulphate occasioned any loss. It will also be seen that the losses of nitrate from solutions containing sodium sulphate were roughly proportional to the amounts of sulphate present, and that important losses were sustained amounting to practically 50 per cent of the nitrate originally present when the larger amounts of the sulphate were used. On the whole the losses from potassium or ammonium sulphates were also proportional to the amounts used, but not so great as in the case of sodium sulphate.

The fact that neither calcium nor magnesium sulphate produced any effect on this determination, while the other sulphates caused losses of nitrate, led to a further investigation of the question. A new solution of sodium sulphate was prepared and used in the same way as above outlined. The results proved to be decidedly different from those previously obtained, the loss of nitrogen being very slight in any case. Subsequent trials showed it to be difficult to secure concordant results when sodium, potassium, or ammonium sulphate was employed, and that only when practically the same conditions of evaporation are maintained, such as the rate of evaporation, temperature, &c., were the results identical.

Lipman and Sharp hold that the loss of nitric nitrogen takes place during the time of evaporation, and consider the loss to be due to the expulsion of nitric acid, brought about by the combined action of heat and the sulphate radical. Theoretically, at the temperature obtained on the water bath no action should take place if the sulphate radical be completely combined in the normal sulphate combination. It was suggested, therefore, that probably the sodium sulphate contained small amounts of the acid sulphate, or that hydrolysis took place to a limited degree, resulting in the formation of small amounts of the acid sulphate.

With the view to throwing some light on this point varying amounts of sodium bisulphate were added to portions of the nitrate solution, evaporated, and the determinations completed as usual.

Effects of Sodium Bisulphate.

$NaHSO_4$ added.	Nitrate N added.	Nitrate N found.
Mgrm.	Mgrm.	Mgrm.
None	0·275	0·275
1·00	0·275	0·195
5·00	0·275	0·047
10·00	0·275	0·003
20·00	0·275	0·003
40·00	0·275	0·005

It will be seen that the acid sulphate under the conditions of these experiments can cause a relatively large loss of nitrates, 10 mgrms. having been found to expel practically all of the nitric nitrogen present. The loss was due to expulsion of nitric acid, as was shown by passing the vapours through a dilute caustic potash solution. Similar results were also obtained with other bisulphates. Therefore, acid sulphates, as might be expected, have the power of setting free nitric acid from nitrates during evaporation on the water-bath.

The expulsion of nitric acid by acid sulphates ought to be preventable by the addition of caustic alkali or carbonate. Experiments on this point showed such to be the case, if sufficient carbonate be added to the solution to completely convert the acid sulphate into normal sulphate. In the following series of experiments sodium carbonate was added to solutions containing different sulphates, and these then added to the nitrate solution, evaporated, and the determination completed as usual. The results are shown in the following table:—

Effects of Sodium Carbonate on the Loss of Nitrate N.

Sulphate added.	Mgrms.	Sodium carbonate added. Mgrm.	Nitrate N added. Mgrm.	Nitrate N found. Mgrm.
None	—	None	0·275	0·270
Na_2SO_4 ..	20	None	0·275	0·185
Na_2SO_4 ..	20	20·00	0·275	0·277
K_2SO_4.. ..	20	None	0·275	0·240
K_2SO_4.. ..	20	20·00	0·275	0·280
$(NH_4)_2SO_4$..	20	None	0·275	0·190
$(NH_4)_2SO_4$..	20	20·00	0·275	0·270
$NaHSO_4$ ..	20	None	0·275	0·006
$NaHSO_4$ ..	20	20·00	0·275	0·280
None	—	20·00	0·275	0·282

From the above data it is shown that sodium carbonate may prevent the loss of nitrates brought about by different sulphates just as would be expected if the loss is caused by the liberation of nitric acid.

In this connection it should be stated that Lipman and Sharp were unable to prevent the loss of nitrates occasioned by sodium sulphate by the addition of sodium carbonate. In the experiments reported above, however, the loss of nitrate during evaporation was entirely prevented by the addition of sodium carbonate. The experiments on this point have been repeated several times, and in no instance was any important loss of nitrate observed when an excess of sodium carbonate had been added to the solution. Indeed it seems difficult to believe that nitric acid could be volatilised and expelled from a carbonate solution under the conditions usually obtaining in this determination.

It is furthermore of interest that no loss of nitrate was observed from the use of sodium carbonate alone. As was pointed out by Chamot and Pratt (*Journ. Am. Chem. Soc.*, xxxiii., 25) carbonates may occasion slight losses of nitrates, due to mechanical causes such as effervescence produced by the reaction of the phenoldisulphonic acid reagent on the carbonates. If sufficient caution be observed, however, such losses may become negligible.

The data submitted in this paper indicate that the making of broad generalisations from specific instances may be entirely unwarranted. The fact that sodium sulphate (supposed to be none other than the normal sulphate) causes a loss of nitrate nitrogen, does not justify the sweeping conclusion that the sulphate radical in any inorganic combination would act in the same way. Although the evidence is of an indirect nature, the above data seem to justify the conclusion that losses of nitrate during evaporation in the presence of sulphates are probably referable to acid sulphates which were either originally present in the solution or perhaps formed by hydrolysis during the evaporation process. The latter view seems the more tenable, since losses took place only in the presence of the sulphates that most easily give rise to the bisulphate.—*Journal of the American Chemical Society* xxxv., No. 6.

A METHOD FOR THE QUALITATIVE ANALYSIS OF THE ZINC GROUP.*

By RICHARD EDWIN LEE, ROY H. UHLINGER, and FRANK O. AMON.

Introduction.

THE investigation reported in this paper is a continuation of the work reported in a previous paper in which it was pointed out that "although it is well known that many of the methods which are generally used in qualitative analysis need revision, apparently very little time has been devoted to the systematic study of their relative effectiveness. It would seem, therefore, that any investigation which comprehended a detailed study of qualitative methods with particular reference to their accuracy in detecting small amounts of the elements in the presence of large amounts of any or all of the elements, and for the purpose of developing and formulating more reliable procedures, would be of considerable value to the analytical chemist." ("A Method for the Qualitative Analysis of the Calcium Group," Richard Edwin Lee and F. L. Mickle, *Orig. Com. 8th Intern. Cong. Appl. Chem.*, i., 257, 278; *Chem. Abstr.*, 1912, vi., 20, 3240; *Chem. Ztg.*, 1912, xxxvi., 1302.)

The purpose of this investigation, however, was the experimental survey of only those methods which are most frequently employed in the precipitation and separation of the metals of the zinc group, namely, zinc, manganese, nickel, and cobalt.

As in the investigation to which reference has been made, "it was hoped that the result of such an examination would render possible the selection of the best of the proposed methods and enable the formulation of the conditions best adapted to securing the desired end. As the work progressed, however, and larger discrepancies among the recommended procedures than had been anticipated were noted, it became obvious that although some methods ought to be revised, others ought to be rejected and new ones substituted, if possible."

Although an effort has been made to formulate such methods as will enable the analyst to estimate the approximate amount of the elements present, care has been exercised in the selection of the final procedures to adopt only those which may be executed with facility by the average worker.

The results of the investigation are reported in the order of their dependence. For convenience in presenting data, the paper has been divided into three parts: "Precipitation of the Group," "Analysis of the Group," and "Summary." Under each of the first two parts there is first presented a "General Discussion," in which the reasons for rejecting certain procedures, and adopting others, are given. This is followed by a record of the "Test Experiments" which were performed to test the accuracy of a given process. Next there is presented the "Procedure and Notes," in which the various details of the adopted procedure are submitted and briefly discussed.

The abreviations used in the cross references may be explained as follows:—G. D. is used for General Discussion; P. for Procedure; N. for Notes; T. E. for Test Experiments.

PART I.—*Precipitation of the Group*: (a) *General Discussion*; (b) *Test Experiments*; (c) *Adopted Procedure*; *Notes*.

(a) *General Discussion*.—With respect to the original precipitation of the members of this group, schemes of qualitative analysis differ as to whether this group and the preceding group (the Iron Group) should be precipitated separately by the successive addition of ammonium hydroxide and ammonium sulphide, or whether these reagents should be added together so that all the elements of the two groups may be obtained in a single precipitate. Authors are about evenly divided on this question of procedure. (Those in Group I. suggest the precipitation of the Iron Group with the Zinc Group; those in Group II., a separate precipitation for each group. Group I.: "Qual. Chem. Anal.," Noyes, A. A.; "Qual. Anal.," Dennis and Whittlesey; "Qual. Chem. Anal.," Noyes, Wm. A.; "Qual. Chem. Anal.," Treadwell, F. P.; "Qual. Chem. Anal.," Stieglitz, Julius; "Qual. Anal.," Baskerville and Curtman; "Anal. Chem.," Menschutkin, N.; "Qual. Chem. Anal.," Perkin, F. M. "Group II.: "Qual. Anal.," Böttger, W.; "Qual. Chem. Anal.," Tower, O. F.; "Qual. Chem. Anal.," Newth, C.; "Qual. Chem. Anal.," Bailey and Cady; "Qual. Anal.," Morgan, W. C.; "Qual. Anal.," Gooch and Walker; "Qual. Anal.," Hill, Arthur E.; "Anal. Chem.," Long, J. H.; "Qual. Chem. Anal.," McGregory, J. F.)

Either method has its advantages as well as its disadvantages. When the two groups are precipitated simultaneously, the problem of the analyst is exceedingly difficult, if large quantities of many of the metals of the two groups are present, and especially so if but traces of only one or two of the members are present. Again, zinc, aluminium, and chromium cannot be completely separated from manganese and iron by alkali hydroxide (Ebler, E., *Z. Anal. Chem.*, xlvii., 665–667; cf. *Chem. Abs.*, 1909, iii., 294—5), the reagent usually employed for this separation when the two groups are precipitated together. Finally, the colour changes which occur during the precipitation of either group and which frequently supply indications as to the presence or absence of certain metals, are partially or wholly obscured when the two groups are precipitated simultaneously.

The objections usually urged against the precipitation of each group separately is that it is difficult to effect a complete separation of the two groups. This difficulty may be nearly overcome by avoiding the use of an unnecessary excess of ammonium hydroxide when precipitating the iron group; or the more elaborate formate, benzoate, or basic acetate methods may be used. If the latter method is employed, phosphates are removed during the regular course of the analysis. Finally, the separate precipitation of the groups renders the analytical problem less complex.

It has seemed advisable, therefore, to adopt the method of precipitating the iron and zinc groups separately.

The next problem presented was the determination of the most reliable group precipitant, *i.e.*, whether ammonium polysulphide, ammonium monosulphide, or hydrogen sulphide should be used. An examination of many of the recommended schemes of analysis revealed the fact that the majority of authors prefer to precipitate the group by use of the reagent "ammonium sulphide." The work conducted in this laboratory, however, indicates that precipitation is most satisfactorily accomplished by hydrogen sulphide. Ammonium polysulphide, $(NH_4)_2S_x$, was rejected for two reasons: First, the sulphides of some of the members of the group, especially nickel sulphide, are markedly soluble in this reagent; second, its presence in the filtrate (from this group) imparts a deep yellow colour and in the subsequent analysis results in the separation of sulphur on standing or heating.

Ammonium monosulphide, $(NH_4)_2S$, as the group precipitant yielded fairly satisfactory results. However, the following objections may be offered to its use: First, nickel is very frequently precipitated in the colloidal condition; second, the shelf reagent, unless freshly made, is a constant source of difficulty, as the monosulphide is readily oxidised in the presence of air to the polysulphide, thus:

$$2(NH_4)_2S + O \rightarrow (NH_4)_2S_x + 2NH_3 + H_2O.$$

Therefore, if a large excess of the reagent is used it is practically equivalent to using the polysulphide.

The method of passing hydrogen sulphide, H_2S, into a weak ammoniacal solution containing the metals of this group presented no new difficulties and practically eliminated the difficulties attendant upon the use of either one

* *Journal of the American Chemical Society*, xxxv., No. 5.

of the two other precipitants. The dissolving of the nickel sulphide is entirely prevented and nickel is seldom precipitated in the colloidal condition.

It would seem, therefore, that the method of precipitating the group with hydrogen sulphide is to be preferred, especially so when nickel is likely to be present. By the procedure outlined in this paper (see Procedure I.) it is easily possible to precipitate as well as detect 0·0005 grm. of any of the metals of this group.

(b) *Test Experiments* (see Note). Series I.—Difficulties Encountered in Attempting to Precipitate Nickel by Ammonium Polysulphide or Monosulphide.

(NOTE.—The record of the "Test Experiments and References" is presented before the adopted procedure is reported. Conclusions drawn from the results obtained in the Test Experiments are incorporated in the "Procedure and Notes.)

After a few trial experiments with $(NH_4)_2S_x$ this reagent was rejected as a possible group precipitant because of its solvent action on nickel sulphide.

When large or small amounts of the pure salts of nickel were used in the test experiments, the complete precipitation of the nickel by the use of ammonium sulphide was found to be almost impossible. The filtrate invariably had a brown colour in each case. When it was boiled for five or six minutes, shaken thoroughly, and then filtered, it usually came through colourless. The amount of nickel in the filtrate apparently increased with the amount of $(NH_4)_2S$ used and the length of exposure to the air.

Lecrenier (*Chem. Ztg.*, 1889, xiii., 431—449), and Villiers (*Compt. Rend.*, 1894, cxix., 1263) have shown, however, that nickel can be completely precipitated as NiS—the filtrate remaining colourless—with freshly prepared $(NH_4)_2S$ in the absence of air. The results obtained by these men indicate that, in those cases to which reference has been made, the brown coloured filtrate is due to the presence of a polysulphide. The composition of this brown coloured filtrate, however, is probably not definitely known. It may be colloidal nickel polysulphide or it may be ammonium sulphonickelate, $(NH_4)_2NiS_3$. Antony and Magri (*Gazz. Chim. Ital.*, 1901, xxxi. [2], 265) prepared NiS_4 by evaporating the brown coloured filtrate in the absence of air.

All the experimental work relating to precipitation of the group with ammonium polysulphide or monosulphide showed that these reagents as possible group precipitants should be rejected.

Series II.—Completeness of Precipitation of Zinc, Manganese, Nickel, and Cobalt in an Ammoniacal Solution with Hydrogen Sulphide.

In the following series of experiments the amount of the metal in the form of a chloride was dissolved in distilled water and diluted to 25 cc., 5 cc. of 5N HCl was added, after which the solution was made *slightly* alkaline with 5N NH_4OH. Precipitation from both cold and hot solution was tried.

A. *Zinc.*

0·0003 grm. Zn (as $ZnCl_2$) gave no precipitate.
0·0004 grm. Zn (as $ZnCl_2$) gave no precipitate but the solution became turbid.
0·0005 grm. Zn (as $ZnCl_2$) gave a distinct precipitate after 1—2 minutes which coagulated perceptibly.
0·001 grm. Zn (as $ZnCl_2$) gave heavy flocculent precipitate.
0·200 grm. Zn (as $ZnCl_2$) gave large precipitate at once and precipitation was complete in 2—3 minutes.

B. *Manganese.*

0·0003 grm. Mn (as $MnCl_2.4H_2O$) gave no precipitate.
0·0004 grm. Mn (as $MnCl_2.4H_2O$) gave no precipitate but the solution became turbid.
0·0005 grm. Mn (as $MnCl_2.4H_2O$) gave a distinct precipitate.
0·001 grm. Mn (as $MnCl_2.4H_2O$), a distinct precipitate was obtained after 1—2 minutes.
0·200 grm. Mn (as $MnCl_2.4H_2O$) gave a heavy precipitate at once and precipitation was complete in 2—3 minutes.

C. *Nickel.*

0·0001 grm. Ni (as $NiCl_2.6H_2O$) gave only a slight colouration.
0·0002 grm. Ni (as $NiCl_2.6H_2O$) gave a distinct precipitate which coagulated perceptibly.
0·0003 grm. Ni (as $NiCl_2.6H_2O$) gave a distinct precipitate.
0·0004 grm. Ni (as $NiCl_2.6H_2O$) gave a distinct precipitate.
0·0005 grm. Ni (as $NiCl_2.6H_2O$) gave a distinct precipitate.
0·001 grm. Ni (as $NiCl_2.6H_2O$) gave a heavy precipitate at once.
0·200 grm. Ni (as $NiCl_2.6H_2O$) gave a heavy precipitate at once and precipitation was complete in 2—3 minutes.

D. *Cobalt.*

0·0001 grm. Co (as $CoCl_2.6H_2O$) gave no precipitate but solution became turbid.
0·0002 grm. Co (as $CoCl_2.6H_2O$) gave a distinct precipitate.
0·0003 grm. Co (as $CoCl_2.6H_2O$) gave a distinct precipitate.
0·0004 grm. Co (as $CoCl_2.6H_2O$) gave a distinct precipitate.
0·0005 grm. Co (as $CoCl_2.6H_2O$) gave a distinct precipitate.
0·001 grm. Co (as $CoCl_2.6H_2O$) gave a heavy precipitate at once.
0·200 grm. Co (as $CoCl_2.6H_2O$) gave a heavy precipitate at once. Precipitation was complete in 2—3 minutes.

This series of experiments shows that quantities as small as 0·0005 grm. of either Zn, Mn, Ni, or Co are precipitated in 2—3 minutes. It is evident, therefore, that the method outlined in Procedure I. provides for a practically complete precipitation of the members of the group.

(c) *Procedure Adopted and Notes. Procedure* I. To the neutral acid solution (or the filtrate of Group III.) containing the elements of the Zinc Group, add 5N NH_4OH until the solution reacts slightly alkaline. Warm the solution, pass H_2S into it for five minutes, shake the mixture and again warm it. Filter at once. Test the filtrate with H_2S to ascertain whether precipitation is complete. If the filtrate has a dark brown colour the presence of colloidal nickel sulphide is indicated. This difficulty may be overcome by boiling this filtrate for 5—10 minutes. This operation coagulates the precipitate, and therefore prevents it from passing through the filter. The nickel sulphide may then be filtered without further difficulty. Wash the group precipitate immediately and thoroughly with an aqueous solution of H_2S. Proceed with the analysis without delay, as the moist sulphides of nickel and cobalt are easily oxidised.

Notes.

(1) If $(NH_4)_2S$ is used to precipitate the group, it mus be freshly prepared, as it oxidises in the presence of ai to ammonium polysulphide, in which it has been shown that NiS is soluble (see T. E., Series I.). The use of a large excess of the reagent $(NH_4)_2S$ is equivalent to the use of ammonium polysulphide.

If hydrogen sulphide is passed into the solution which is made slightly alkaline with 5N NH_4OH all of the difficulties enumerated are overcome and no new difficulties are presented.

(2) A large excess of ammonium hydroxide is to be avoided when the solution is made slightly alkaline preparatory to its treatment with H_2S, as the excess will be converted into $(NH_4)_2S$ and probably into $(NH_4)_2S_x$. On the other hand great care must be exercised to keep

the solution slightly alkaline in reaction during the precipitation with H_2S.

(3) It has been shown (T. E., Series I.) that the brown coloured filtrate is due to the presence of $(NH_4)_2S_x$, which exerts a solvent action upon NiS. This colloidal nickel salt may be coagulated by boiling and shaking and then removed by filtration.

(4) Precipitations from cold ammoniacal solutions were as satisfactory as those from warm solutions if the amounts of the metals were greater than 0·001 grm.

(5) The precipitation of the metals of this group is practically complete (see T. E., Series II.).

(To be continued).

ON THE

PREPARATION AND PROPERTIES OF THE AMMONIUM SALTS OF SOME ORGANIC ACIDS.*

By LeRoy McMaster.

Most of the ammonium salts of organic acids described in the literature consist of a molecule of the ammonium salt combined with a molecule of the free acid in the case of monobasic acids, while, in the case of dibasic acids, the ammonium salt described is generally an acid ammonium salt. They were usually prepared by neutralising an aqueous solution of the acid with ammonium water or ammonium carbonate, and the solution allowed to evaporate to crystallisation. Many of the salts thus formed also contained water of crystallisation.

In attempting to prepare some diammonium salts by the above method, Keiser and McMaster (*Am. Chem. Journ.*, xlix., 84) always obtained the acid salts. They then dissolved the organic acids in absolute alcohol or ether and conducted into the solution a stream of dry ammonia gas. White crystalline salts were precipitated. In this manner they prepared the ammonium salts of fumaric, maleic, mesaconic, and citraconic acids, which, upon analysis, proved to be the diammonium salts. Ammonium salts of malonic acid and *o*-phthalic acid were also prepared, but were not analysed.

I have continued this work on the dibasic acids, and have prepared the neutral ammonium salts of malonic, succinic, malic, tartaric, *o*-phthalic, and *m*-phthalic acids. The method was applied also to the preparation of the ammonium salts of some monobasic acids—propionic, isobutyric, palmitic, benzoic, and cinnamic. Some of the properties of these ammonium organic salts have also been studied. All of the acids used were obtained from Kahlbaum, except the tartaric acid, which was Baker's analysed product.

Ammonium Malonate.—Finkelstein (*Liebig's Ann. Chem.*, cxxxiii., 338) attempted to make the neutral ammonium salt of malonic acid by adding an excess of ammonia water to an aqueous solution of the acid, and allowing the mixture to evaporate over lime. The liquid lost ammonia, and finally became acid. The acid ammonium salt crystallised out. I have prepared the neutral salt of malonic acid by the method described by Keiser and McMaster, but with some difficulty. If ammonia gas is conducted into an ethereal solution of the acid until no further precipitate is formed, the salt will be found not to be neutral. Analysis of two samples of the salt thus prepared gave respectively 16·65 per cent and 16·62 per cent of nitrogen. The acid ammonium salt of malonic acid contains 11·57 per cent of nitrogen, and the neutral salt 20·29 per cent nitrogen. It is thus evident that each of these preparations was a mixture of the acid ammonium salt and the neutralt salt. In this experiment dry ammonia was conducted into an ethereal solution of 5 grms. of malonic acid for about one half-hour. However, if the ammonia is run into a solution of 5 grms. of malonic acid for about three hours and allowed to come in contact with the precipitated salt, the neutral ammonium malonate is formed. The salt thus prepared is a white crystalline powder, not deliquescent but readily soluble in water. The aqueous solution is neutral. The salt, on analysis, gave the following results :—

N calculated for $CH_2(CO_2NH_4)_2$	20·29
Found—I.	20·3
II.	20·26

The first nitrogen determination was made by the Dumas method, the second by the Kjeldahl method.

Ammonium Succinate.—Berzelius states in his *Lehrbuch der Chemie* that the salt which results from the evaporation of a neutral solution of ammonium succinate is an acid salt. By adding an excess of ammonia to a solution of succinic acid and allowing the liquid to evaporate, Doepping (*Liebig's Ann. Chem.*, xlvii., 253) obtained a salt that was easily soluble in alcohol, and not deliquescent. He concluded that he had a neutral salt. Fehling (*Ibid.*, xlix., 154) found that the neutral salt could not be so easily prepared, and that the salt obtained by the method of neutralisation and evaporation is either an acid salt or a mixture of the acid and neutral salts, especially if ammonia is used in excess. He obtained the neutral ammonium salt by adding to basic lead acetate an excess of a solution of neutral ammonium succinate and evaporating in a vacuum over sulphuric acid the mother-liquor. As soon as the mass was mostly crystallised out, it was washed with a little water to remove traces of lead, pressed between filter-paper, and dried at 40—50°. Fehling thus obtained the neutral ammonium succinate in crystalline form.

Dry ammonia gas was run into an alcoholic solution of succinic acid, and a white crystalline powder was formed which was not deliquescent in the air but dissolved readily in water. The aqueous solution was neutral to sensitive litmus-paper. The salt is only very slightly soluble in alcohol, and was washed on the filter with alcohol and ether. The salt can also be prepared by conducting the ammonia into an ethereal solution of succinic acid. The salt prepared in absolute alcohol gave, on analysis, the following results :—

N calculated for $(CH_2CO_2NH_4)_2$.. ..	18·42
Found—I...	18·36
II...	18·38

Prepared in ether :—

N found	18·38

Ammonium Malate.—No record can be found of the preparation of neutral ammonium malate. The acid malates have been made and extensively studied by Pasteur (*Liebig's Ann. Chem.*, lxxxii., 331) and Bremer (*Ber.*, xiii., 352). When ammonia gas is run into an alcoholic solution of malic acid, there is first formed a white mucilaginous substance which soon changes to a crystalline powder. Analysis proved this salt to be a mixture of ammonium acid malate and the neutral malate. The neutral salt was prepared by passing the gas into a solution of 5 grms. of the aid for several hours, the salt filtered off by suction, washed with alcohol and ether, dried in a desiccator, and then placed in a dry flask, filled with ammonia, and tightly stoppered. The flask was shaken at intervals, and portions taken out from time to time and tested for neutrality. It was found necessary to allow the salt, prepared as described above, to stand in contact with the ammonia for three days in order to become neutral. The compound thus prepared was very slightly deliquescent, and dissolved readily in water. Determinations of nitrogen by the Kjeldahl method gave :—

* Presented before the St. Louis Academy of Science, February 17, 1913. From the *American Chemical Journal*, xlix., No. 4.

N calculated for $C_4H_4O_5(NH_4)_2$		16·66
Found—I...		16·64
II...		16·63

Ammonium Tartrate.—Tartaric acid was dissolved in absolute alcohol and ammonia gas passed into the solution until a portion of the salt on being dissolved in water showed a neutral solution. When the ammonia was first passed in a white curdy precipitate formed. This soon changed to an amorphous powder which, as soon as neutral, was filtered by suction on an alundum crucible, and washed with alcohol and ether. The salt is not at all deliquescent, and is very slightly soluble in alcohol. Analysis gave the following result:—

N calculated $C_4H_4O_6(NH_4)_2$..	15·21
Fonnd	15·19

Ammonium o-Phthalate. — Marignac (*Liebig's Ann. Chem.*, xlii., 215) describes the preparation of this salt by the action of liquid ammonia on the acid. This salt was precipitated from an alcoholic solution of *o*-phthalic acid by dry ammonia, filtered by suction on an alundum crucible, washed with alcohol and ether, and dried in a desiccator. It is a fine white powder, soluble in water, scarcely soluble in alcohol. The salt is not deliquescent.

N calculated for $C_6H_4(CO_2NH_4)_2$ . ..	14·00
Found	13·98

(To be continued).

THE SCIENTIFIC WEEK.

(*From Our Own Paris Correspondent*).

Toxic Fish with Venomous Milts.

Although venomous fishes have long been known, what are much less known are those whose glands contain poisons capable of provoking poisoning, and that only at a certain period of the year. Since 1882 Russian and Japanese doctors have taken up this question, after having observed symptoms of poisoning after the ingestion of fish coming from the coast of Nippon and belonging to the species *Tetradon* and *Orthagoricus*. The toxins are in the head, liver, and especially the milts and roes of these fish; while the flesh is absolutely inoffensive and may be consumed without the slightest inconvenience. The toxic effect seems to be specially localised in the ovaries and testicles of these fish, other species of which are to be found in the waters of the Cape and New Caledonia. The venomous matter does not exist on account of the putrefaction of these organs, which are toxic even when in an absolutely fresh state. Several observations of poisoning have been reported from the ingestion of certain fish of Asiatic rivers, the glands of which as well as the flesh, when once ingested, bring on gastro-intestinal troubles, collapse, and death. The flesh becomes inoffensive after cooking, whereas the eggs and the milt remain toxic after lying six months in alcohol. The toxin of the *Tetradon* is principally to be found in the ovaries, and this explains the frequency of the accidents during the spawning season in April and May. The toxin paralyses the animals experimented upon and appears to have a particular affinity for the bulbous centres. It does not seem to be an organised ferment nor an inorganic base. In fact all the searchers are agreed as to the seat of this poison; the liver and the testicles are generally less toxic than the ovaries, and the muscles rarely contain any noxious principle. Heat can destroy this toxin, but the ebullition must be prolonged for three hours at least to obtain its perfect destruction. At the time of spawning there is normally a special morbid alteration that is the veritable cause of the poisonous nature of the glanduary organs of these fishes. The maximum of toxicity coincides with the maximum of the activity of the glands. This phenomenon is analogous to that observed in the muscles of overtaxed animals; the muscles of hunted animals become real poisons. Up till now no poisonous fishes have been met with on the coast of France. The accidents that have been observed in Europe after the ingestion of fish were due either to a state of putrefaction or to the bacillary infections of these animals.

M. A. J. Albahary has made most interesting researches on this subject, but it would be interesting if analytical chemists were to try and determine in a precise manner the nature of this noxious and venomous principle in the glands.

Dwarf Plants and Monstrous Flowers.

M. J. A. Urbain, Professor of Chemistry at the Sorbonne, has had the idea of making seeds germinate after having deprived them of their albumen. Thus, by his own will, he obtains monstrous vegetables. His work is returned in a paper read before the Academy of Sciences by the eminent Professor of Botany, M. Gaston Bonnier. Evidently the albumen of a seed is not its essential part; albumen is only an alimentary reserve destined to feed the young plant until its radicle has become strong enough to seek for its food itself. But can the young plant do without this alimentary reserve? M. J. A. Urbain shows that, if put to the test, it can do so, but not without suffering from the privation. M. Urbain's experiments have been made with seeds of the Palma Christi, the poppy, &c. These seeds deprived of their albumen germinated like normal seeds, but produced dwarf, stunted plants with modified leaves and often monstrous deformed flowers. This research of M. Urbain goes to prove the possibility of creating monstrous plants at will. In the same way way the late Camille Daresle produced, at will, monstrous chicken by interfering with the normal evolution of the egg, either by varnishing a part of its surface, or by exposing it to a too strong heat, or by tormenting it in some other manner.

The Microbe of Hydrophobia Discovered.

A discovery of extreme importance, which will mark its date in the history of bacteriology, has just been made by Prof. Hideyo Noguchi, the learned Japanese who has made so many researches concerning syphilis. Noguchi has just simply discovered the invisible microbe of hydrophobia. In an article just published in the *Presse Medicale* the learned Japanese describes the method that has enabled him to see the nucleated round or oval corpuscles that seem to be the infectious agents of hydrophobia. Galtier and Pasteur have shown that hydrophobia is infectious. Other learned men, as Remlinger, Volpino, Poor, Steinhardt, have shown the filtrability of the virus of rabies, but the nature of the virus itself had remained unknown. It was in the beginning of 1912 that Noguchi undertook the culture of the virus of rabies. He has made about fifty series of cultures with the brain or the marrow taken aseptically from rabbits, guinea-pigs, and dogs to whom the virus of rabies had been transmitted. In these cultures he reproduces the tiny granulous corpuscles of the hydrophobic virus which are to be found at the limit of microscopic visibility. The method employed to cultivate these infinitely small microbes and to render them visible is that which has been employed for the culture of the spirochetes of recurrent fever. The appearance of these corpuscles was sudden and abundant and of a duration of four or five days. These cultivated corpuscles do not look like bacteria but like protozoa. Noguchi has made his controlling experiments at the Rockefeller Institute of New York, where he has his laboratory. With the cultures containing these granulous corpuscles he has inoculated dogs, rabbits, and guinea-pigs, who all in a short time showed the typical symptoms of rabies. Prof. Noguchi's discovery will throw a new light on the very obscure problem of filtering microbes, and open new horizons to bacteriological science.

Wireless Telegraphy Stations.

At the present moment there exist on the surface of the globe 230 radiotelegraphic stations open to the public; they are to be found in the following places:—Canada 32, England 25, Russia 22, Germany 20, Italy 20, Brazil 16, East Indies 11, Spain 9, and France only 8. Over the different seas of the globe 1200 mercantile vessels are navigating provided with wireless telegraphy. Here, again, France with 90 vessels comes far behind England (590) and Germany (253). The majority of French ships provided with apparatus for free communication belong to the two ports of Marseilles (46) and Havre (29). However, it is to be remarked that Marseilles, although possessing more than half the ships provided with wireless telegraphy apparatus, has, as yet, no central station, and from this point of view is tributary to the station of Sainte-Marie-de-la-Mer, from whence the radio-telegrams are transmitted by telephone. To indicate the development of this new mode of communication and the necessity of endowing Marseilles with a central station it suffices to give the number of messages received: 22 in 1908, 2393 in 1910, 6151 in 1911, 8217 in 1912. These figures are sufficient without further comment.

The Last Two Comets.

M. Chauffardet, of Besançon, has just made a study of the last two comets that approached our world in 1913. The last is quite recent. Russian astronomers took it for a planet of the eleventh magnitude, and thought they had made a fine discovery. It was, however, a false joy. It was an old acquaintance—a periodical comet that has come to visit us for the third time since 1889. Its periodicity is then only of eight years. This, for a comet, is but a very small orbit, which accounts for its having been taken at first for a planet. The mistake is explained by the presence of a very small nucleus with very distinct outlines, and which was visible before the appearance of the tail.

The Olfactory Sense of Insects.

A great number of facts of the life of insects can hardly be explained excepting by admitting a particularly powerful olfactory sense in these animals. The examples are numerous; if, in an ant hill, an ant of the same species as those that inhabit it, but belonging to another swarm, tries to penetrate, it will immediately be expelled. Sometimes the hypothesis has been supposed of a sort of language allowing each individual to make itself known, but deafness is general in the class of insects, and ants in particular are absolutely deaf. So then there only remains the odour special to each swarm which appears to constitute a mode of identification. In the same way, when the corpse of a small mammiferous animal is becoming decomposed in a field, a legion of sylphs and necrophors, strangers to the immediate neighbourhood, coming sometimes from a distance of several kilometres, arrive to lay their eggs there, guided, it would seem, merely by their sense of smell. It is also their scent which leads the sacred scarabeus to the excrements of herbivorous animals, of which it will make a ball in which to place its progeniture, &c. But is it really scent that guides the insect? Very little is known on the subject; the only precise experiments are due to Fabre, the learned entomologist of Serignan, to whom are due those marvellous studies on the life of insects that he has so well related in his "Entomological Mémoires." The starting-point of these experiments was the sexual attraction in butterflies, well known to entomologists, which enables individual insects to meet in spite of the often considerable distance and difficulties of the way. Fabre enclosed females of different species of butterflies in a metallic trellis, and found that numerous males arrived. A remarkable particularity of these experiments was that one of the specimens studied had very rarely been observed in the region. On the contrary, if the females were shut up under an hermetically closed glass globe the attraction ceased, but all objects, branches, stuff, paper, on which they had rested for some time was seen to be possessed of the same attractive properties. Fabre has concluded from these results that a particular odour exists incapable of affecting our sense of smell, but which can be transmitted to a great distance. Although it is bold to generalise, it seems possible to admit that insects are endowed with a wonderfully strong olfactory sense which no other animal possesses.

Ernest Solvay and Soda.

The Jubilee of Ernest Solvay that has just been celebrated in Belgium has drawn attention to one of the most important chemical industries—that of soda. J. B. Dumas said that the two greatest novelties of the nineteenth century were the steam-engine and artificial soda, which may be considered as the staff of chemical industry. A century ago soda was obtained by the calcination of certain plants, and Spain, who was the greatest producer, exported into France more than 30 millions of soda. But in 1793 the blockade closed all the French frontiers, and the want of Spanish soda was so strongly felt by French industry that the Republic made an appeal to all citizens who had establishments, or who had obtained patents, for obtaining soda from sea salt. Nicholas Leblanc's process was seen to be the only practical one, and the inventor generously and patriotically made his invention public. This saved French industry, but poor Leblanc was ruined, and losing his wits through distress and poverty he committed suicide. Eighty years later 500,000 tons of soda, worth 80 millions of francs, were manufactured annually by his process! It was accidentally in mixing carbonate of ammonia with sea salt, that Solvay noticed the formation of soda. He patented the process in 1861, but it was only in 1865, after the invention of the carbonator column, that the process became profitable and made the fortune of its inventor. In 1865 the factory of Couillet produced 400 kilogrms. of soda a day, 1500 kilos. in 1866, and 3000 in 1867. Since that time the production by the Solvay method has steadily increased. In France, in 1875, the enormous factory at Dombasle was established, producing 250,000 kilogrms. a day. Then came the manufactories of Sandbach in England, of Wylen and Bernbourg in Germany, of Bereneski in Siberia, and Syracuse in America, which employ 800 directors and 12,000 workmen. The Solvay factories produce 1,700,000 tons of soda a year out of a total mundane consumption of 1,800,000 tons. Thanks to this process the price of soda has gone down from £5 a ton in 1860 to 24s. in 1868 and 10s. in 1882.

NOTICES OF BOOKS.

Water Purification and Sewage Disposal. By Dr. J. Tillmans. Translated by Hugh S. Taylor, M.Sc. London: Constable and Co., Ltd. 1913.

This critical survey of modern methods of water purification and sewage disposal deserves a warm reception at the hands of sanitary authorities in England, who will find that in all respects it is thoroughly up to date. The purification of drinking water on the small and large scales is first discussed, and the advantages and disadvantages of different methods are clearly and concisely exhibited. Various processes for water softening for technical purposes are considered in a short chapter. The purification of sewage by biological and other means is then described, and the disposal of industrial sewage is fully treated. The effluents of some thirty different industries are considered separately and in some detail, and the results of recent investigations are discussed.

Tables Annuelles de Constantes et Données Numériques de Chimie, de Physique, et de Technologie. ("Annual Tables of Constants and Numerical Data, Chemical, Physical, and Technological"). Paris: Gauthier-Villars. London: J. and A. Churchill. 1913.

VERY few alterations have been found necessary in this second volume of numerical tables beyond bringing all information down to the latest possible date. The data included in the chapter on the Properties of Mixtures have now been distributed in suitable places throughout the text, and in some cases English weights and measures have been replaced by those of the metric system. The explanations are usually in French, but the indexes and titles are printed in English, French, German, and Italian, and technical and collegiate libraries in these four countries will find the book invaluable.

Forty-ninth Annual Report on Alkali, &c., Works. By the CHIEF INSPECTOR. London: His Majesty's Stationery Office. 1913.

THE forty-ninth annual report on alkali, &c., works contains the detailed reports of the work of the district inspectors, together with a discussion of them by the Chief Inspector. The number of registered works in the country shows a net increase of 9, and on the whole the chemical industry exhibited great activity during the year 1912. The report also contains further details of the investigation of the behaviour of oxide of iron during fouling and revivification, which was considered at some length in the preceding report.

The Cane-sugar Factory. By FREDERIC J. SCARD, F.I.C. London: The West India Committee. 1913.

THIS little book provides, at a very moderate price, a brief guide to the processes of milling, clarification, filtration, &c., employed in a cane sugar factory. It is written in the form of question and answer, and the study of it will excellently prepare the beginner for the use of more advanced works. While no attempt is made to go deeply into scientific principles, the practical methods employed are clearly outlined, and a complete glossary of the terms used in cane-sugar practice is given, together with some useful numerical tables, including a concentration table showing the percentage of water evaporated between given densities.

An Investigation of the Coals of Canada. By J. B. PORTER, E.M., D.Sc., and R. J. DURLEY, Ma.E. Vol. VI. Ottawa: Government Printing Bureau. 1912.

THE sixth volume of the report of the investigation of Canadian coal which has been conducted at the McGill University, Montreal, contains Appendix IV. on the manufacure and testing of coke, and Appendix V. on the work of the chemical laboratory. In the latter details are given of the analyses of coal samples undertaken in the laboratory, and some weathering tests are described. A paper on the spontaneous combustion of coal by Dr. E. Stansfield, M.Sc., read before the Canadian Mining Institute is also reproduced. It contains a summary of the literature of the subject down to the year 1910, and discusses some cases of spontaneous combustion which have occurred, and also the remedial measures which have been or may be adopted.

E. Merck, Chemical Works, Darmstadt, Germany. London: E. Merck, 66, Crutched Friars. July, 1913.

THE name of Merck is now fully recognised as a guarantee of the purity and absolute reliability of a chemical, and the firm has always been in the vanguard in the manufacture of all classes of pharmaceutical preparations. In the latest list of chemicals one of the most important additions is Fibrolysin, a remarkable solvent for scar tissue, which is now quoted for the first time.

Graham Flour. By J. A. LE CLERC and B. R. JACOBS. Washington: Government Printing Office. 1913.

THIS *Bulletin* of the Bureau of Chemistry of the U.S. Department of Agriculture contains the Report of a careful study of the differences between the physical and chemical properties of true and imitation Graham or whole-wheat flour. The authors have found that many millers have long been in the habit of making a so-called Graham flour by mixing low grade flour and bran in suitable proportions, and by a great number of comparative experiments with different samples they have discovered what determinations must be made in order to ascertain whether a given flour is genuine or otherwise. These determinations relate chiefly to the quantity and character of the intermediate products and to the amounts of fibre, ash, and pentosan, which are always less in imitation than in true Graham flours.

Gas Analysis. By L. M. DENNIS. New York: The Macmillan Company. 1913.

THE text of this book is based upon the English translation of Hempel's "Methods of Gas Analysis," but it is practically a new work, for the great advances in methods of analysing mixtures of gases which have been made during the last few years, and the many new pieces of apparatus which have been devised for special purposes, are all duly described. The processes included for description are chiefly those which are useful in rapid technical analysis. General methods and the manipulation of gases are treated fully in the early part of the book, and a chapter on the construction of apparatus contains practical hints which will be of great value to those who are not experienced in work of this kind. The theory and practice of the determination of gases by combustion are well explained, and de Voldere and de Smet's laws of the combustion of gases are summarised. The properties and determination of the various gases which are of technical importance and of mixtures of them are then described, and the analysis of atmospheric air, illuminating gas, &c., is discussed in detail.

Protection of Intellectual Property. By Dr. L. H. BAEKELAND.

THIS pamphlet contains the Presidential Address, delivered by Dr. Baekeland before the Meeting at Detroit of the American Institute of Chemical Engineers in December, 1912, which has been reprinted from the *Journal of Industrial and Engineering Chemistry*. In it Dr. Baekeland puts forward an eloquent plea for the need of widening the Patent Laws and educating the public in a rational and equitable view of the importance of the reform of the whole patent system. He takes into consideration chiefly chemical patents, as being the most difficult to protect from infringement, and although he claims that on the whole the American Patent Laws are the best, he has many suggestions to offer for improving them. The Oldfield Bill he regards as likely to have far-reaching and dangerous effects. Possibly the most valuable of his proposed improvements is based upon the German system, by which the burden of technicalities and expert knowledge is thrown upon the Patent Office, or a Court connected with it, which with a Court of Appeal would constitute an efficient machinery for adjudicating the title and validity of patents, lessen the cost of administrating the laws, and encourage a healthy inventive activity among poor men as well as those who have large means at their disposal.

L'Année Electrique. ("The Electrical Year"). By Dr. FOVEAU DE COURMELLES. Paris: Ch. Beranger. 1913.

THIS book contains a review of progress in electricity, electrotherapy, and radiography during the year 1912. A great many results are brought together in it, especially

as regards the medical use of electricity, while recent advances in the applications of electricity in traction, lighting, &c., are shortly described. Those who want a semipopular account of electrotherapy will find it in the book, which also gives full references to periodical literature on the subject.

Cours Élémentaire de Chimie et de Minéralogie. ("Elementary Course of Chemistry and Mineralogy"). By Dr. C. I. Istrati and Dr. G. G. Longinescu. Second French Edition. Translated by A. Adam. Paris: Gauthier-Villars. 1913.

The inductive method of learning chemistry is advocated in this book, which will give the student a satisfactory grounding in the subject, and enable him to profit by the subsequent use of more advanced works. In the early chapters the authors proceed always from the known to the unknown, and the consideration of the atomic theory is deferred until the student has acquired a fair knowledge of some of the common elements and their more important compounds. On the other hand, the deductive method is not altogether discarded, but is effectively employed in the latter part of the book which deals with organic chemistry. Many experiments, mostly such as are easy to perform with simple apparatus, are described, and technical applications are in many cases given some prominence. A good deal of attention is paid to mineralogy, and the book is wonderfully comprehensive, containing a large amount of matter which is logically presented to the reader and thoroughly well arranged.

Einführung in die Spektrochemie. ("Introduction to Spectrochemistry"). By G. Urbain. Translated by Dr. Ulfilas Meyer. Dresden and Leipzig: Theodor Steinkopff. 1913. (Mk. 9).

The most important facts and theories of elementary spectrochemistry are very well summarised in this book, and Prof. Urbain has at his command a lucid and graphic style which should be much appreciated by those who are beginning the study of the subject. The elementary theory of light and the formation of the spectrum are treated in introductory chapters, which lead up to a detailed account of the technique of the production of spectra. Many diagrams of apparatus are reproduced, and full descriptions of experiments are given. The theory of electrochemistry is also shortly treated from an elementary point of view; much new work on phosphorescence done by Prof. Urbain is described, and a few good plates of spectra are included. The German translation follows the French original very closely, the only alterations which have been made being the addition of some recent results and of some references to German literature.

OBITUARY.

DR. JULIUS LEWKOWITSCH.

We much regret to have to report the death of Dr. Julius Lewkowitsch, which occurred on September 16th at Chamonix, after a short illness. Dr. Lewkowitsch was born in Prussian Silesia in 1857, and studied at Breslau under Prof. von Richter. After obtaining the degree of Doctor of Philosophy he remained at the University doing research work, in which his marked originality won for him great success. He afterwards became assistant to Dr. Landolt at the Berlin Agricultural High School, and subsequently assistant to Prof. Victor Meyer at Heidelberg. At this period Meyer was actively engaged in the investigation of problems in stereochemistry, and Lewkowitsch worked on the same subject, publishing many original papers. His life work, however, may be regarded as the development of the industries connected with Oils and Fats, and in the course of time he became the world's greatest authority upon the subject. He was the author of a standard treatise on "Oils, Fats, and Waxes" (London, 1898), which has been translated into English and German, and he also wrote "A Laboratory Companion to the Fats and Oils Industries" (London, 1901), and translated Benedikt-Ulzer's work "Analyse der Fette und Ole."

Dr. Lewkowitsch was a valued member of the Councils of the Chemical Society, the Society of Chemical Industry, and the Institute of Chemistry, which owed much to his administrative talents and his wide knowledge of technological problems.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Atti della Reale Accademia dei Lincei.
Vol. xxii. [i.], No. 11, 1913.

New Decomposition of Oximes.—A. Angeli and Luigi Alessandri. — At 180° benzophenoxime undergoes rapid decomposition according to the equation $3C_{13}H_{11}NO = 3C_{13}H_{10}O + NH_3 + N_2$. The silver salt of the same compound decomposes at the ordinary temperature, regenerating benzophenone and liberating nitrogen. The yield of nitrogen obtained in one experiment was about 40 per cent of that calculated from the equation $C_{13}H_{10}NOAg = C_{13}H_{10}O + Ag + N$. Other oximes, *e.g.*, piperonal oxime, undergo the same reaction which is analogous to that of hydroxylamine:— $3NH_2OH = NH_3 + N_2 + 3H_2O$.

Thorium Molybdates.—A. Barbieri.—Neutral ammonium thorium molybdate, $(NH_4)_8Th(Mo_2O_7)_6.8H_2O$, can be obtained by adding a solution of anhydrous thorium sulphate to a solution of ammonium heptamolybdate and heating. The amorphous white precipitate first formed changes in appearance and becomes crystalline. The corresponding sodium salt can be prepared similarly. The acid salt, $(NH_4)_6H_2Th(Mo_2O_7)_6.11H_2O$, is prepared by adding to a nitric or hydrochloric solution of ammonium thorium molybdate a solution of ammonium nitrate, sulphate, or chloride. The solutions of alkaline thorium molybdates in dilute acids give the following reactions:— With salts of Ca, Rb, Cs, K, Sr, a white crystalline precipitate. With salts of Ba, Pb, Tl, Hg'', Hg' a white amorphous precipitate. No precipitate with salts of magnesium or zinc. With salts of cadmium in concentrated solution a crystalline precipitate. With salts of aniline in concentrated solution a crystalline compound, which contains six atoms of nitrogen to one of thorium, and which is probably an acid thorium molybdate of aniline.

Compounds of Hydrated Salts with Organic Bases. —F. Calzolari.—The hydrated dithionates of Mg, Mn, Fe, Co, Ni form well-defined crystalline addition compounds with caffeine and hexamethylene tetramine, and with the latter the hydrated sulphates and thiosulphates of the same metals form similar compounds. The author has prepared and investigated a large number of these compounds, typical formulæ of which are:— $MgS_2O_6.8H_2O.2C_8H_{10}.N_4O_2$, $MgS_2O_6.6H_2O.2C_6N_4H_{12}$, $MgSO_4.9H_2O.C_6N_4H_{12}$, $MgS_2O_3.8H_2O.C_6N_4H_{12}$.

MEETINGS FOR THE WEEK.

Wednesday, 15th.—Microscopical, 8. Conversazione at King's College.

The Historical Medical Museum.—In response to numerous requests it has been decided to defer the closing of the Historical Medical Museum until October 31st. During the month of October it will remain open from 10 a.m. to 6 p.m. daily, and from 10 a.m. to 1 p.m. on Saturdays. After this date it will be closed for a few months for rearrangement as a permanent Museum. It is proposed to reopen the Museum in its permanent form in the spring of next year.

THE CHEMICAL NEWS.

VOL. CVIII., No. 2812.

THE GLOW OF SULPHUR.

By W. H. WATSON.

ALTHOUGH not mentioned in the majority of text-books, the fact that sulphur under certain circumstances exhibits a glow or "phosphorescence" has been frequently recorded. The method of obtaining the glow was described by Berzelius in his "Lehrbuch" (5th edition, vol. i., p. 185), and since then several investigators have turned their attention to the matter, but without arriving at an explanation of the phenomenon. The idea has been suggested that the glow was accompanied by the formation of a lower oxide of sulphur, possibly a monoxide, SO, but attempts to obtain such a body by Heumann (*Ber.*, xvi., 139), O. Jacobsen (*Ber.*. xvi., 478), and also by the writer, have proved unsuccessful. Experiments upon the oxidation of sulphur at low temperatures by Moissan (*Comptes Rendus*, 1903, xxxvii., 547) also lend no support to the idea. At the suggestion of Prof. H. B. Baker, to whom the writer desires to express his indebtedness, a further investigation of the phenomenon was undertaken with the results set forth below.

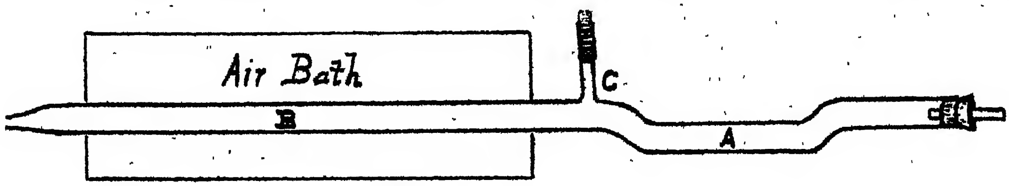
In the paper by Heumann referred to above, the author describes various methods of obtaining the glow, the most successful of which appears to be that of placing sulphur on a shallow tray supported above the bottom of an iron air-bath heated to about 240°, and allowing a current of air to pass over the molten sulphur. When the conditions are properly regulated, a large flame, differing in colour from the usual blue flame of burning sulphur and also in the fact that it is relatively cold (see also Baker, *Journ. Chem. Soc. Trans.*, 1900, lxxvii., 646), can be obtained and maintained for a considerable time. The author states that the slow combustion is accompanied by a curious smell which he compares to ozone or camphor.

These facts have been confirmed by the present writer, who found that the glow invariably exhibited itself as a curious luminous flicker over the heated base and adjacent parts of the sides of the oven, but never on the surface of the sulphur. Further experiments were made by means of an apparatus similar to that described below.

A piece of glass tubing, 40 to 50 cm. long and about 1 cm. bore, was bent as shown in the sketch, and had a narrow side-tube sealed in at C. Some pure re-crystallised sulphur, which had previously been kept melted for some time, was placed in the part A, while B was enclosed in an air-bath kept at 100—120° C. The sulphur was maintained at about 250°, while a slow current of pure dry air was passed through the apparatus, the side-tube C being closed. So long as the sulphur was kept below its ignition-point, no luminosity could be observed on the surface of the sulphur, but the air current became charged with a cloud of fine particles which were carried along the tube and not completely deposited before reaching the open end. In the portion of the tube within the air-bath, extending for some centimetres from the end nearer the melted sulphur, a steady glow could be observed, which, however, ceased if by any chance the liquid sulphur became ignited. The glow could be produced at any part of the tube B by heating gently at that part and allowing the rest to remain cool, even when B was of considerable length. By using a mixture of nitrogen and air a somewhat brighter glow was obtained, but the glow completely ceased if pure nitrogen were employed. In this latter case, however, it was possible to obtain a glow by introducing air through the side-tube C. It would therefore seem unlikely that the glow is connected with a preliminary action of oxygen on the heated sulphur.

If the air current after passing over the heated sulphur were filtered through a tube filled with recently ignited asbestos no glow whatever could be obtained in B, but the glow reappeared when the asbestos was removed. Similar results were obtained if cotton-wool or pieces of moist stick potash were used instead of asbestos. Bubbling the air through water was also effective, and a quantity of colloidal sulphur collected in the water.

In another series of experiments the gases escaping from the end of the tube in which the glow was taking place were led through a tube immersed in liquid air. A small amount of solid sulphur dioxide was collected, and in some cases a liquid. This latter, however, contained no sulphur compound other than a trace of sulphur dioxide, as on careful evaporation and bubbling the resulting gas through fuming nitric acid or a solution of potassium permanganate, no sulphuric acid was obtained. The gas contained about 40 per cent of free oxygen, and the residue appeared to be nitrogen and probably some argon. Similar results were obtained if the gases immediately after leaving the heated sulphur, and without allowing the glow to occur, were treated in the same way. In all cases the gas which escaped liquefaction by the liquid air was quite odourless.



There is therefore no direct evidence that an appreciable amount of an oxide of sulphur other than dioxide is formed at any stage. Heumann arrived at a similar conclusion from an analysis of the gases escaping from glowing sulphur. The glow appears to be caused by the oxidation of the particles of finely-divided sulphur resulting from the cooling of the air which has passed over the heated sulphur, and this view is in harmony with the observations recorded both here and in the records of earlier investigators. If this finely-divided sulphur is the result of some such reactions as the following — $2S+O_2=2SO$, then $2SO=SO_2+S$, the intermediate product must have a merely transient existence, and its presence would not be shown by chemical tests.

The finely-divided sulphur not only undergoes oxidation at a comparatively low temperature, but attacks copper and silver at the ordinary temperature with the production of black films of sulphide. Experiments made in order to discover whether the particles were electrified or not failed to show the existence of a charge. Air containing the finely-divided sulphur led through a tube containing an insulated piece of copper-foil connected with a delicate electroscope did not discharge the latter, whether the instrument carried a positive or negative charge. In other experiments the stream of finely-divided sulphur passed between two long strips of platinum foil, insulated and connected to opposite terminals of a small induction coil. Some 5 to 10 mgrms. of sulphur deposited on the plates in the course of an hour, but although the amounts deposited on the two plates were generally unequal, the variation

was not large, and, moreover, not constant. On the whole the results obtained were not decisive.

Summarising the results obtained, it may therefore be stated that when air passes over sulphur heated to a temperature below its ignition-point, the air becomes charged with sulphur vapour, which, as the temperature falls, separates as a mist or cloud of very small particles. The oxidation of this finely-divided sulphur gives rise to the phenomenon of the glow or "phosphorescence," but there is no evidence that at any stage any other oxide than sulphur dioxide is formed.

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SOME CURIOUS ATOMIC WEIGHT RELATIONS: QUATERNIAN SERIES.

By F. H. LORING.

REFERRING to my letter in the CHEMICAL NEWS (vol cviii., p. 95), may I call attention through your columns to a further extension of the quaternian series therein indicated.

It was shown that (1) argon, iron, bromine, and silver form a series in which the secondary differences in atomic weight stand in geometrical progression, these being 4 : 8 : 16 (argon taken twice), and their sum 28 (4×7). That (2) thallium, in some respects, resembles the alkali metals and silver, and appears to form the eligible end-member of a parallel series, namely, "9·75," cobalt, iodine, and thallium, the secondary atomic weight differences being 9·3, and 18·6, their sum 28 (4×7). It was shown that the differences approximate very closely to these values.*

It is now suggested that *helium*, *aluminium*, *manganese*, and *rubidium* form a similar series, in which the sum of the secondary differences may be taken as 7. The parallelism in certain chemical properties with the above elements of higher atomic weight is somewhat strained, yet upon a little study it will be seen that these elements seem singularly related to each other. Fresenius places aluminium and chromium together, and it is known that "aluminium is isomorphous with iron in the ferric state." (Tilden—"The Elements," 1910—points out this connection between aluminium and iron, and a periodic table is given in which iron is shown as a direct descendant from aluminium). Manganese appears to be heptavalent in Mn_2O_7, as is probably the case with chlorine in Cl_2O_7, whilst potassium permanganate is isomorphous with potassium perchlorate, with which it crystallises in all proportions, thus identifying this element with the halogens. Rubidium and thallium form some compounds which are isomorphous with each other. The relations are thus made apparent. The new series is as follows :—

	At. wts.	Differences.	
He	= 3·98		
		23·15	
Al	= 27·13		4·66 (*b*)
		27·81	
Mn	= 54·94		2·33 (*a*)
		30·14	
Rb	= 85·08		

Experimental value, 85·45.

$2a = b$; $a+b = 7$.

The atomic weights employed throughout these studies are, for the most part, those harmonised by a scheme of elliptical curves (CHEM. NEWS, 1909, xcix., 148), rubidium being shifted so as to fall in the central part of the chart or tabular scheme to agree in position with its analogues, since the alkali metals form a group of elements more nearly alike than, perhaps, those of any other regular group of active members; if any irregularities in this respect exist this group should show it, although other groups do not in the system cited. This element so placed does not fall on a curve, but the positions of all the curves are not fixed. Such is my view, at any rate.

The value, 85·08, is slightly lower than the present accepted experimental figure, 85·45, but since rubidium appears to be radio-active in that it emits a feeble radiation (β-rays), it is possible that it may be contaminated with an appreciable amount of another element of higher atomic weight, which is radio-active. It is true that the absence of α-rays seems to preclude the possible presence of a well known radio-active element as an impurity, because the only known radio-elements of long period which emit β-rays give rise to, or are ultimately followed by, an α-ray product. No α-rays have been detected in the case of rubidium (see Rutherford, "Radio-active Substances and their Radiations," 1913, pp. 587—590).

Since the α-rays are rapidly ejected helium atoms, which belong to the even valency series (0—2—4—6), it is strange that some member of the odd valency series, such as hydrogen, is not likewise expelled, if only slowly, especially in connection with radio-elements belonging *properly* to the odd series (1—3—5—7), assuming that such radio-elements exist. Radium D, or actinium E (end-product), might have the value 210·43, which differs from the value "211·43" by exactly one whole unit, but it is not to be inferred that hydrogen atoms are emitted from the hypothetical impurity of rubidium, yet the idea has an experimental suggestion in it. The quoted value is of another series given below.

Attempts to allocate neon (20·00) at the head of a series have not been very successful. Nickel (58·66), though chemically beyond cobalt (59·00), is numerically below this element in position. Similarly, but in a reverse sense, tellurium (127·50) stands chemically before iodine (126·92), but numerically beyond this element.

The assumption that these chemically active elements are the nearest higher analogues, in one case in chemical position, and in the other in numerical place, leads to an extrapolated value, 211·43, which should be an analogue of silver or rubidium, or even thallium, and which by analogy might be an irregularly placed element in the Periodic Table. If I may offer a suggestion, such an element might be radio-active, and it might even be the impurity possibly present in rubidium.

It should be remembered that Sir J. J. Thomson has found an impurity in the purest neon thus far obtained, which fact, though not itself justifying the lower atomic weight above given, permits the use of the lower value with some reason, especially since this value is in harmony with many others adjusted by the system referred to above. The doubtful series is as follows :—

	At. wts.	Differences.	
Ne	= 20·00		
		38·66	
Ni	= 58·66		30·18 (*b*)
		68·84	
Te	= 127·50		15·09 (*a*)
		83·93	
?	= 211·43		

(These elements appear to have closely associated neighbours:—"21·7," Co, I, "210·43 ?," and these are apparently the *regular* ones).

$2a = b$; $a+b = 45·27$.

The number of intervening active elements shows a fairly uniform progression, as is the case with the other elements singled out by this particular treatment (see CHEMICAL NEWS, cviii., 95).

There is one more series of doubtful character.

Mendeleeff predicted an inactive gas having an atomic weight of about half that of hydrogen (0·4). Several attempts to work out definite values have been made.

* The values employed were—107·9, 79·9, 55·9, 39·9, 39·9, 204·17, 126·92, 59·00, 9·75, 21·7 by further extrapolation, which may be J. J. Thomson's neon associate "22." (See last table).

The value 0·27 (see CHEMICAL NEWS, 1909, c., 281) is here tried as a head member of a quaternian series, but it is exceedingly doubtful whether this value is the right one, assuming the existence of such an element.

A series beginning with the above value in question can be arranged if *boron*, *magnesium*, and *potassium* be taken. On account of the radio-activity of the last-named element its *true* atomic weight, like that assumed in the case of rubidium, might be less than the present experimental value. The following table shows an attempt to bring into relation the atomic weights of these elements; this arrangement has some support from the regular progression of the intervening chemically active elements, nitrogen being taken as an inactive gas, which, in its diatomic state, it remembles:—

Intervening elements.	At. wts.	Differences.	
	? = 0·27		
3		10·73	
	B = 11·00		2·550 (b)
4		13·28	
	Mg = 24·28		1·275 (a)
5		14·55	
	K = 38·83		

Experimental value, 39·09.

(38·83 + 0·27 = 39·10, but this coincidence in values can hardly be regarded as significant).

$$2a = b\,;\ a+b = 3·825.$$

Boron has properties which identify it with aluminium, bearing in mind that it is the first member of Group III., since initial or terminal members of a group usually show deviations from the characteristics common to members which comprise the major portion of the group.

Strong resemblances between Groups III., IV., and VIII., which may be regarded as being made up of branch members joining or forming part of the seventh group, are traceable through certain elements which exhibit characteristics common to these groups.

Magnesium certainly does not seem to be very closely related to manganese, but perhaps a careful comparative study of these two elements will reveal likenesses. Quoting from Senter's "Inorganic Chemistry" (1911, p. 527): "*Manganese* and the halogens are the only known members of the seventh group. The former element, like those belonging to the sixth group just considered, forms compounds belonging to a variety of stages of oxidation, and shows analogies with *magnesium*, iron, chromium, and other elements, as well as the halogens." The italics are mine.

It is perhaps of interest to note that the decimal fractions of the values a and b are so related to the whole numbers that if the latter be represented as a_i and b_i, and the decimal fractions corresponding with these values be represented as a_f and b_f, then the equality of the ratios—

$$\frac{a_i}{a_f} = \frac{b_i}{b_f},$$

obtains in each case where fractions exist. This, of course, may be an accidental coincidence.

The following table shows the elements brought into special relation with each other by this method. In the table 0·27 = A′, 21·7 = B′, 9·75 = C′, and 211·43 = D′.

	A′ ?		B		Mg		K	
	He		Al		Mn		Rb	
[Ar]		Ar		Fe		Br		Ag
[B′]		C′ ?		Co		I		Tl
	Ne		Ni		Te		D′ ?	

This table appears to reconcile the value 21·7, and the duality of argon is made apparent, whatever this may mean. Has this peculiarity any connection with the probable fact that RaEm and AcEm are substantially or exactly the same in atomic weight?

These curious relations lead me to think that they are worth careful study, but whether they can be relied upon as devices for the adjustment of atomic weights, or as methods of extrapolation, is open to question. *Experiment only can determine this.*

Apart from the question of the ultimate utility of these methods, they do, in my opinion, point the way for certain lines of experiment, as, for example, the search for a radio-element in rubidium having chemical properties allied to thallium, or some element immediately beyond bismuth.

The elements gold, mercury, thallium, lead, and bismuth seem to embody some of the characteristics possessed by lower group members (these qualities being additional to other qualities which give them their higher place in the Periodic Table), as if, in some way, they, more than other elements, were the sweepings which included the fragments of materials intended for higher homologues of the lower groups.

CONNECTION BETWEEN BOILING-POINT AND MOLECULAR WEIGHT OF BODIES.

By J. C. THOMPSON.

III.

IT was shown (CHEMICAL NEWS, cvi., 178) that $\frac{T}{\sqrt{\rho}}$ is an approximate multiple of a constant, T representing the boiling-point of a liquid, ρ representing the density of its vapour.

This relationship, though holding fairly well for most inorganic bodies, for the more complex organic bodies gives figures differing widely from the constant. While attempting to extend the formula in order to include these organic bodies a remarkable relationship was discovered. This relationship is of extreme interest with regard to double bonds. The relationship becomes clear on evaluating—

$$\frac{T}{\rho_L^{0·235}\,M^{0·5}}$$

for hydrocarbons. $M^{0·5}$ *the* $\sqrt{\textit{molecular weight}}$ *has replaced* $\sqrt{\rho}$ as a more convenient number.

ρ_L is, as in Part II., the density of the body in the liquid state.

A rough correction is made in the final column to allow for the temperature at which the density is measured.

For every 1° C. of inaccuracy in boiling-point an average error of 0·1 in the factor results.

From these figures it is obvious that the greater the proportion of double and triple bonds in the molecule the greater the value of the function—

$$\frac{T}{\rho_L^{0·235}\ \ ^{0·5}}.$$

Thus:—

(1)	Acetylene has its function of value ..	44·95
	Ethylene „ „ „ ..	40·8
	Ethane „ „ „ ..	40·4
(2)	Toluene gives	41·0
	Tetrahydrotoluene gives	40·1
	Hexahydrotoluene gives	39·5
(3)	Metaxylene gives	41·2
	Dihydro metaxylene gives	40·3
	Tetrahydro metaxylene gives	39·2
	Hexahydro metaxylene gives	39·2

That the formula—

$$\frac{T}{\rho_L^{0·235}\,D^{0·5}}$$

Formula.	Boiling-point, T.	Density, ρ_L.	Molecular weight, M.	$\frac{T}{\rho_L^{0·235} M^{0·5}}$.	$\frac{T}{\rho_L^{0·235} M^{0·5}}$ estimated for ρ at 0° C.
H—C≡C·H (acetylene)	190	0·45 at 0° C.	26	44·95	44·95
CH:C.CH_2.CH_2.C:CH (dipropargyl)	358	0·81 „ 20° C.	78	42·6	42·2
C_6H_5C≡CH	415	0·9295 „ 20° C.	102	41·4	41·0
C_2H_4	170	0·361 „ 0° C.	28	40·8	40·8
$C_6H_5CH=CH_2$	417	0·9074 „ 20° C.	104	41·8	41·3
C_6H_6 (benzene)	353·5	0·874 „ 20° C.	78	41·4	41·0
$C_6H_5CH_3$	383	0·869 „ 16° C.	92	41·3	41·0
$C_6H_5C_2H_5$	407	0·876 „ 10° C.	106	41·6	41·4
$C_6H_4(CH_3)_2$ (orthoxylene)	415	0·8932 „ 0° C.	106	41·4	41·4
$C_6H_4(CH_3)_2$ (metaxylene)	412	0·8812 „ 0° C.	106	41·2	41·2
$C_6H_4(CH_3)_2$ (paraxylene)	412	0·881 „ 0° C.	106	41·2	41·2
$C_6H_3(CH_3)_3$ (mesitylene)	437·5	0·90 „ 0° C.	120	41·0	41·0
$C_6H_4(C_2H_5)_2$ (meta)	455	0·8602 „ 20° C.	134	40·7	40·2
$C_6H_6(CH_3)_2$ (orthodihydroxylene)	406	0·828 „ 20° C.	108	40·8	40·3
$C_6H_6(CH_3)_2$ (metadihydroxylene)	392	0·814 „ 20° C.	108	40·8	40·3
$(CH_3)_2C:CH_2$	267	0·637 „ 14° C.	56	39·7	40·0
C_2H_6 (ethane)	183	0·446 „ 0° C.	30	40·4	40·4
C_3H_8	235	0·536 „ 0° C.	44	41·0	41·0
C_4H_{10}	274	0·600 „ 0° C.	58	40·6	40·6
C_5H_{12} (normal)	309	0·633 „ 15° C.	72	40·6	40·3
C_5H_{12} (iso)	301	0·627 „ 15° C.	72	39·6	39·3
C_7H_{16}	371	0·700 „ 0° C.	100	40·3	40·3
$C_{10}H_{22}$	446	0·745 „ 0° C.	142	40·1	40·1
$C_6H_9CH_3$ (tetrahydrotoluene)	377	0·797 „ 18° C.	96	40·6	40·1
$C_6H_8(CH_3)_2$ (metatetrahydroxylene)	392	0·794 „ 14° C. 0·814 „ 0° C.	110	39·5 39·2	39·2
C_6H_{12} (hexahydrobenzene)	343	0·7473 „ 0° C.	84	40·1	40·1
C_7H_{14} (hexahydrotoluene)	368	0·7723 „ 0° C.	98	39·5	39·5
C_8H_{16} (hexahydrometaxylene)	391	0·781 „ 0° C.	112	39·2	39·2
C_8H_{16} (para)	410·6	0·7956 „ 4° C.	112	40·9	40·8
$C_3H_7C_6H_{11}$	421	0·787 „ 20° C.	126	39·7	39·2
$CH_3C_6H_{10}C_3H_7$	445	0·8116 „ 17° C.	140	39·5	39·1

is the completely correct form is highly improbable as it is not deduced from theoretical considerations. But that boiling point, density as liquid, molecular weight, and degree of saturation are nearly related in this manner can be readily seen.

IV.

A theory which can explain the influence of double bonds will now be put forward. The carbon atom is supposed to possess four valencies placed so that if the carbon atom be at the centre of a tetrahedron each valency is in the direction of one of the corners. Now these valencies are treated by Baeyer in his tension theory as though of a semi-rigid nature capable of bending when subjected to strain. It appears, however, far better to consider these valencies as possessing the properties of forces of attraction. A double linkage becoming the resultant of two of these forces. A triple linkage becoming the resultant of three of these forces.

Now with four equal forces placed in this manner the resultant of two or three of them is obtained by mathematics. Thus if each force be considered equal to f, the resultant of two of them $= \frac{2}{3}\sqrt{3}f = 1·155$, the resultant of three of them $= f$.

Consider now the three bodies:—(1) Ethane, (2) ethylene, and (3) acetylene.

The forces connecting their carbon atoms together are, in the first case, for each carbon atom f, in the second case $1·155 f$, in the third case f. In the second and the third a portion of the valency forces possessed by the carbon atoms has not been used, for a normal carbon atom should possess forces amounting in value to $4 f$. In the second case the force value $= 3·155 f$. In the third case the force value $= 2 f$.

Thus in the second case there is for each carbon atom a force of $0·845 f$, and in the third of $2 f$ not used within the molecule. By "being used within the molecule" is meant neutralised by other forces within the molecule. Now, any forces of attraction not used within the molecule, owing to there being no matter within the molecule to act upon, will be used in attracting neighbouring matter. The normal saturated molecule attracts neighbouring molecules, and is kept from neighbouring molecules by its kinetic energy. The unsaturated molecule will be attracted with a greater force than the saturated.

It has been shown (see Part II.) that $\rho_L \frac{T}{m}$ varies as A, where A is the attractive pressure exerted at the boiling-point of the liquid.

Now, from the kinetic theory ρ_L varies directly as the pressure; temperature remaining constant. Similarly, temperature varies directly as the pressure; density remaining constant. That is to say, that an increase in pressure will have the same effect upon the density as it has upon the temperature.

Now, in the expression—

$$\frac{T}{\rho_L^{0·235} M^{0·5}},$$

it is required to find the effect of an increased attractive force. Owing to the nature of the force producing the increase in attraction it will be independent of the molecular weight. Also, since T for increase of attraction varies in the same manner as ρ_L, the expression—

$$\frac{\rho_L}{\rho_L^{0·235}}$$

will vary in the same way as—

$$\frac{T}{\rho_L^{0·235} M^{0·5}}$$

with respect to attractive pressure. But—

$$\frac{\rho_L}{\rho_L^{0·235}} = \rho_L^{0·765}.$$

Since ρ_L increases with pressure, $\rho_L^{0.765}$ increases with pressure; that is, the expression—

$$\frac{T}{\rho_L^{0.235} M^{0.5}}$$

increases in value when there is an increase in the attractive forces of the molecule, or the forces due to the unsaturation of the molecule increase the value of the expression—

$$\frac{T}{\rho_L^{0.235} M^{0.5}}.$$

NOTE ON CHEMICAL NOMENCLATURE.

By GERALD HARGRAVE MARTIN.

Chemists call the compound HgS mercuric sulphide or sulphide of mercury, but they never refer to it as sulphur mercuride. At first sight the reason for this custom is not obvious. When two elements combine they disappear, and a new substance with different properties appears in their place. Empedocles attributed the properties of substances to his metaphysical elements, or principles, which were carried by one original matter; and under Aristotle's care this view became widely accepted.

While this view prevailed there was no reason why the names of the disappearing substances should be included in the name given to the substance which appears in their place. Thus, when Geber prepared mercury sulphide artificially, he called it usifur.

During the middle ages the metaphysical elements became replaced by material elements; thus the metaphysical sulphur and mercury of Geber became materialised into brimstone and quicksilver, and during the iatro-chemical period it became realised that cinnabar was composed of these two substances. After the chemical revolution the balance reigned supreme in chemistry, and the properties of compounds were attributed to their ponderable composition. The elements were generally supposed to continue to exist in their compounds, although in a disguised form.

In what order should the names of the elements appear in those of their compounds? The modern chemist has no logical reason for regarding either element in a binary compound as being of greater importance than the other. To the alchemist, however, the metals were by far the most important substances; thus there were noble metals resembling that most noble and perfect metal gold; there were base metals; there were bastard metals; and, lastly, there were non-metallic substances. Beside their monetary value the metals have played a most important *rôle* during our civilisation. Thus the stone ages were followed by the bronze age, and we are still living in the iron age.

Now it is the miserable non-metallic elements which combine most readily with the metals, so who could hesitate as to which element should have the place of honour in the name of the compound? You might say sulphuret or sulphide of mercury, or mercury sulphide, but it was not meet to say mercuride of sulphur, or sulphur mercuride.

Hence the name of the metal occupied the place of honour in the name of the compound, for were not the metals the most important things in inorganic nature? The chemists inherited this custom of honouring the metals from the alchemists; the terms noble and base metal have survived. Mercury sulphide is described in the text-books under the compounds of mercury, and not under the compounds of sulphur; its formula is written HgS and not SHg. In compounds which contain no metal the more positive element or radical, which apes a metal in the compound, was presumably from force of custom given the place of honour. Thus, water was hydrogen monoxide, or oxide of hydrogen, but was never called oxygen hydride; CS_2 was carbon bisulphide, not sulphur carbide.

Although, after Lavoisier's chemical revolution, oxygen played a most important *rôle* in chemical theory it could not have the place of honour in the names of its compounds, for it was the least metal-like or most electronegative element known. Thus, although chemists wrote of chloride of nitrogen, and not of nitride of chlorine, the compounds Cl_2O, ClO_2, &c., were called oxides of chlorine, and not chlorides of oxygen. This custom has also been generally observed in organic chemistry; CH_3I is called methyl iodide, not iodine methyl. Although in the compound $C_2H_5—S—C_2H_5$ the sulphur is regarded as binding the two ethyl groups together, the compound is always called ethyl sulphide, never sulphur ethide.

The positive radicals, however, had to cede the place of honour to a genuine metal; thus, although $(C_2H_5)_2S$ was ethyl sulphide, $(C_2H_5)_2Zn$ was zinc ethyl, but not ethyl zincide. We find the rule observed even in the Grignard compounds such as magnesium methyl-iodide, although the names magneside of methyl iodide, or iodine methyl magneside, would be just as logical.

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NEW RESEARCHES ON LIQUID CRYSTALS.*

By O. LEHMANN.

If two solid crystals of the same substance in different orientation are brought into contact with one another, they remain unaltered. On the other hand, two liquid crystals flow together and endeavour to assume the same structure as is shown by the alteration of the orientation of the optical anisotropism. Thus the molecules of the liquid crystals are mobile, but their arrangement is not quite irregular as in ordinary liquids; they exert a directive force upon one another, like magnets which are free to move, or rather like astatic magnetic systems (see O. Lehmann, "Die neue Welt der flüssigen Kristalle," 1911, 346).

This mobile state of equilibrium remains unchanged as long as the external conditions which influence it are unaltered. After any disturbance which is not too deep-seated it returns to its original condition when the external conditions again become the same. Only in rare cases does the arrangement of the molecules correspond to the grating structure of ordinary solid crystals. Usually only the axis about which the molecules easily turn is parallel for all molecules, while the secondary axes, perpendicular to it, take up all possible positions, which continually alter. This semi- or pseudoisotropic structure (*loc. cit.*, p. 196 *et seq.*) is midway between that of homogeneous solid crystals and that of homogeneous non crystalline liquids. Very frequently, however, the structure is not even homogeneous; discontinuity of structure, the formation of twins, sphaerolithic and fan-like groupings of the chief axes of the molecules, conical disturbances, &c., occur, as has already been mentioned in earlier researches.

The essential properties of crystalline liquid substances, like melting, solidification, and transition points, solubility, vapour tension, &c., are unaffected by these modifications of the molecular arrangement; thus there is no transition to another "phase." Alterations of anisotropism cannot be explained on the hypothesis that matter is continuous, and thus they are proofs of the existence of molecules.

But even on the basis of existing molecular theories the possibility of such mobile equilibria of the molecules cannot be deduced. They constitute a perfectly new physical fact, which, if it can be satisfactorily explained, must necessarily lead to important results as regards molecular forces. But even if the explanation is not forthcoming this new fact is of importance, inasmuch as it considerably

* Abridged from *Sitzungsberichte der Heidelberger Akademie der Wissenschaftung*, 1913, A, xiii.

limits the number of possible molecular hypotheses. Accurate empirical investigation of the facts is obviously what is now required in this region.

The flowing together of two crystals to form a single crystal was observed for the first time in the modification of ammonium oleate called "Schmierseife" (*Zeit. Phys. Chem.*, 1895, xviii., 91; "Die neue Welt der flüssigen Kristalle," p. 175). On account of some objections which have been put forward (see A. Mlodziejowski, *Zeit. f. Kristallogr.*, 1913, lii., 1) I have extended these observations.

I.—*The Preparation of Liquid-crystalline Ammonium Oleate.*

Herr Mlodziejowski recommends the following method (*loc. cit.*, p. 1):—"The oleic acid was mixed with much aqueous ammonia in a test-tube, the liquid was poured off the precipitate, and the latter was dissolved in ethyl alcohol." Now it is not impossible to obtain thus a preparation which forms liquid crystals, but it is not the same as those investigated by me, as I shall presently show, and usually no result is obtained. For if much ammonia is really used no precipitate with a superincumbent liquid results, but only a turbid colloidal solution (soap water) from which no precipitate settles even after it has stood for some time. In any case, the method is faulty because a preparation which is too rich in water is obtained. If preparations are used which are evaporating freely as Herr Mlodziejowski recommends, and from which the alcohol is escaping more rapidly than the water, the error is still greater. No excess of water must be present, *i.e.*, the proportions of water and ammonia must be correctly chosen. This is impossible if the oleic acid is treated with commercial ammonia.

As I have previously stated, to obtain the preparation it is best to pass ammonia gas from a steel cylinder into oleic acid till it smells strongly of ammonia (Note 1). Thus a neutral anhydrous oleate ammonium is obtained. If this is fused under a cover-glass on a slide (care being taken that no bubbles arise owing to decomposition), and the cooling is watched under a microscope, it is seen that the mass solidifies as a whole to small needle-shaped (rhombic?) crystals of a labile modification. These are soon converted into a rather less fusible stable modification appearing as imperfectly formed (monoclinic?) leaflets. From alcoholic solution these latter can be obtained as relatively large crystals with sharp edges. If the crystalline mass is rubbed up with a trace of water, without the addition of alcohol (Note 2), and after previously warming it, the process of crystallisation is watched, it is observed that this is not a single process as before; it is seen that liquid crystals first separate, and after some time these are absorbed by the small needle-like crystals or the stable leaflets. The process can be followed still better in presence of alcohol. If the concentration is not uniform the leaflets crystallise out after some time in the regions of greater concentration. These regions are bordered by a zone filled with labile needles and appearing less light (grey) through crossed Nicols. Outside this second zone there is a third zone of liquid crystals which by flowing together may form individuals of considerable size. The limits of the zones gradually spread outwards, and after waiting a little it will be seen that the whole has been transformed into the leaflet modification (Note 3). The greater the amount of water added the more the quantity of liquid crystals increases at the expense of the solid, but the tendency to change into the latter is smaller.

Herr Mlodziejowski (*loc. cit.*, p. 3) disputes the correctness of my statement that the liquid crystals are absorbed by the solid crystals. The discrepancy is easily explained, for Herr M. did not employ my method for preparing the substance, but a simpler method, as described above, in which he did not obtain the anhydrous solid crystals of neutral ammonium oleate observed by me. Thus he was working with another substance.

Taking into account the fact that he speaks of a precipitate from which the superincumbent liquid was poured off, and which consisted of drops of oleic acid with a stiff crust of soap, it may be assumed that his preparations contained not only water but also oleic acid in excess, so that the solid crystals observed by him were crystals of acid ammonium oleate hydrate. These naturally do not absorb the liquid crystals of neutral ammonium oleate hydrate, for they are not polymorphic modifications of the latter.

An anhydrous acid ammonium oleate does not exist. Solid neutral ammonium oleate certainly dissolves in oleic acid (as in alcohol), but it crystallises out again unchanged. If some water is added the different shaped much larger crystals of the acid hydrate separate from the solution; they can also be obtained by rubbing up the liquid-crystalline ammonium oleate hydrate with a sufficient quantity of oleic acid (by means of a spatulum on a sheet of glass). The oleic acid completely disappears if the right amount is used, and the mass which was previously liquid-syrupy becomes wax-like and solid. If oleic acid is present in excess, or if some alcohol is added as solvent, the substance is covered with a cover-glass shaped like a clock-glass, warmed, and then allowed to cool, crystals of this acid hydrate of ammonium oleate can be obtained. They possess remarkable shapes owing to the frequent occurrence of fan-shaped structural disturbances (see the photographs in the author's book "Flüssige Kristalle," 1904, Table I., Figs. 1—3 and Figs. 4—6, and Table II., Figs. 1—3, 5; the substance is not an absorption compound of neutral oleate with oleic acid, or a solid solution in the former, as was previously stated). If the quantities of oleic acid and water were originally insufficient they may be obtained in addition to the solid anhydrous crystals of the neutral ammonium oleate. A mutual disturbance naturally does not occur any more than in presence of liquid crystals. As was to be expected the liquid crystals can be obtained from them by the addition of ammonia.

We shall now return to the original experiments. If we continue to add water to the solid anhydrous crystals of ammonium oleate it may easily be seen under the microscope that when the amount of water has reached a certain definite limit the whole mass is converted into the syrupy liquid-crystalline modification. Thenceforward no needles or leaflets of the anhydrous modification appear; the mass has become neutral ammonium oleate hydrate. The chemical change can easily be followed macroscopically if some of the anhydrous mass is mixed by means of a small spatulum on a glass plate with more and more water. The water completely disappears, and finally the mass becomes uniform and is now no longer solid and waxy as originally, but liquid and syrupy. At the moment at which the last traces of leaflets disappear we have the pure liquid crystalline modification.

The same observation can be made with a solution of the anhydrous modification in alcohol. In this case also the continued addition of small quantities of water causes the appearance of liquid crystals, and after the addition of the right quantity only the latter crystallise out. Instead of pure water it is better in all cases to use water saturated with ammonia, as the ammonia present cannot do any harm, and may prevent the hydrolytic decomposition of the ammonium oleate (Note 4).

The fact that the hydrated liquid-crystalline modification crystallises out unchanged from anhydrous alcohol is a proof that the water is not water of crystallisation but firmly combined hydrate water, for absolute alcohol usually absorbs the water of crystallisation from salts containing it.

This stability of liquid crystals towards alcohol and other solvents makes it possible to purify them by recrystallisation like solid crystals. For instance, the ammonium oleate is rubbed up in a porcelain dish, kept warm by means of a water-bath, until a clear solution is obtained, and then this is poured into a closed separating funnel, and allowed to cool. After some time the solution becomes turbid owing to the separation of isolated small crystals. These gradually sink to the bottom, and form a

thick deposit just like a turbid but translucent deposit, consisting of solid crystals which separates from other solutions. The liquid-crystalline layer can then be separated by pouring off the mother-liquor, but it is not possible to effect complete separation because the crystals are always mixed with some alcohol.

Notes.

1. (*Ann. d. Phys.*, 1906, xxxi., 183. The chemical factory of E. Merck, Darmstadt, supplies a preparation specially for the demonstration of liquid crystals at 5.10 Mk. for 100 grms.; the raw oleate at 1.65 Mk. for 1 kgrm. can also be used. If a solution is required in order to prevent the mass getting stiff, which makes it difficult to pass the ammonia through, alcohol is added to the oleic acid; this partly dissolves the oleate so that a fairly liquid paste is obtained.

2. It is sufficient to leave the preparation uncovered for some time, when it absorbs moisture from the air, or to breathe on it.

3. For this reason I have previously suggested that the liquid crystals may be a labile modification of ammonium oleate which could be preserved by the addition of suitable substances. Closer investigation has shown that this suggestion is not correct. The chief effect of the addition of any substance is produced by the water it contains. Thus if anhydrous ammonium oleate and the syrupy liquid crystalline modification are brought together on a slide under a cover-glass and warmed till fusion occurs, the leaflets which form on cooling do spread somewhat into the liquid-crystalline (partly semi-isotropic) mass, but only as far as the latter contains anhydrous oleate mixed with it or dissolved. Possibly the liquid crystals separating in such mixtures can be regarded as mixed crystals with the anhydrous oleate, which is also suggested by the fact that they show only a very slight tendency to flow together.

4. According to Kraft and Stern, *Ber.*, 1894, xxvii., 1755, no basic oleic acid salts are formed.

(To be continued).

ON THE

PREPARATION AND PROPERTIES OF THE AMMONIUM SALTS OF SOME ORGANIC ACIDS.*

By LeROY McMASTER.

(Concluded from p. 183).

Ammonium m-*Phthalate.*—On passing ammonia gas into an alcoholic solution of *m*-phthalic acid a very voluminous white gelatinous precipitate was formed, which changed to a white powder. The salt was filtered by suction, and washed with only a small amount of alcohol, as it is somewhat soluble in this medium in the absence of the ammonia. The complete precipitation of this salt in alcohol depends, therefore, upon an excess of ammonia. Ammonium *o*-phthalate, on the other hand, is quite insoluble in alcohol. It was impossible to prepare ammonium *p*-phthalate by this method on account of the insolubility of *p*-phthalic acid in both alcohol and ether.

The ammonium *m*-phthalate was dried in a desiccator, and, on analysis, gave:—

N calculated for $C_6H_4(CO_2NH_4)_2$	14·00
Found	13·96

The method having proved so very applicable in the preparation of neutral ammonium salts of dibasic acids, it was next tried on the preparation of neutral ammonium salts of monobasic acids. Some work is in progress in the Washington University on the preparation of neutral salts of tribasic acids by the same method.

Ammonium Propionate.—When ammonia gas was first passed into an ethereal solution of propionic acid, no precipitate formed. White fumes came off which condensed in the top of the flask to a beautiful snow-white substance. After the gas was passed in for a short time, a white voluminous precipitate formed. The precipitate was quickly filtered by suction, washed with ether, placed in a vacuum desiccator for a few minutes, and then in a calcium chloride desiccator. The salt deliquesces very readily, and is very soluble in water. On first dissolving the salt in water, the solution is neutral. The solution, however, soon turns acid, due to hydrolysis. The salt is very soluble in methyl alcohol, ethyl alcohol, and acetic acid. Analysis proved it to be the neutral ammonium propionate.

N calculated for $C_2H_5CO_2NH_4$	15·38
Found	15·4

Ammonium Isobutyrate.—Isobutyric acid was dissolved in ether, and ammonia passed into the solution. A snow-white precipitate of lustrous appearance formed. This was filtered by suction, washed with ether, and dried in a desiccator. Though not deliquescent, the salt cannot be dried in the air, for it has a very high vapour tension. An appreciable quantity of the salt will disappear entirely in a short time if exposed to the air. The salt is soluble in alcohol and water. The aqueous solution is neutral. Determination of nitrogen by the Kjeldahl method gave:—

N calculated for $C_4H_7O_2NH_4$	13·33
Found	13·32

Ammonium Benzoate.—By evaporating a solution of benzoic acid neutralised with ammonia there is obtained an acid salt of the formula $NH_4C_7H_5O_2.C_7H_6O_2$ (Berzelius). The neutral salt can be obtained by conducting ammonia gas into an ethereal solution of benzoic acid. A white gelatinous precipitate was formed, which, after being filtered and washed with ether, dried in the air to an amorphous powder. It is not deliquescent, but soluble in water, in which it shows a neutral reaction. The salt is somewhat soluble in ethyl alcohol, from which it can be crystallised. Analysis proved it to be the neutral ammonium benzoate.

N calculated for $C_6H_5CO_6NH_4$	11·02
Found	11·02

Ammonium Cinnamate.—When ammonia gas was passed into an ethereal solution of cinnamic acid a white gelatinous precipitate at first formed which turned to an amorphous powder. It was necessary to pass the gas into the solution for several hours in order to obtain the neutral salt. The salt is soluble in water and is not deliquescent in the air. If the salt is crystallised from alcohol, beautiful white crystals are formed which have a marked odour of oil of cinnamon. The original salt prepared in ether has no such odour. Also, the salt crystallised from alcohol is very much less soluble in water than the original salt. Ammonia was passed into an alcoholic solution of cinnamic acid, and there were formed at once glistening white crystals. After the ammonia was passed into the solution for some time, the alcohol was poured off from the crystals into a crystallising dish, and allowed to evaporate spontaneously. A further quantity of the crystals was obtained. These crystals, prepared from the alcoholic solution of the acid, had an odour of oil of cinnamon, but not so marked as in the case of the salt prepared in ethereal solution and afterwards crystallised from alcohol. The crystals prepared in alcohol were again found to be much less soluble in water than the amorphous powder prepared in ether. Determination of nitrogen in the salt prepared in ether gave the result:—

N calculated for $C_9H_7O_2NH_4$	8·48
Found	8·49

Action of Ammonia on Palmitic Acid.—When dry ammonia gas was passed into an ethereal solution of palmitic acid there was produced at once a very voluminous

* Presented before the St. Louis Academy of Science, February 17, 1913. From the *American Chemical Journal*, xlix., No. 4.

white gelatinous precipitate. The precipitate did not become crystalline even after passing in the gas for three hours. The precipitate was filtered by suction and washed with ether. It dried in the air to a white substance resembling a "soap." It was soluble in alcohol, especially if the alcohol was warm. Ammonia was also passed into an alcoholic solution of palmitic acid for three hours. No precipitate formed at first, but as the ammonia gas continued to pass into the solution a precipitate was formed which after a while dissolved, and again after a short time re-precipitated. The precipitate and alcoholic solution were poured into a crystallising dish and the alcohol allowed to evaporate. While wet with alcohol the precipitate was granular in appearance, but after the alcohol had entirely evaporated and the compound became dry, it had the appearance of the compound prepared in ether. The compound prepared in each case was evidently an ammonium "soap." It was not analysed.

This investigation is being continued with other organic acids.

A METHOD FOR THE QUALITATIVE ANALYSIS OF THE ZINC GROUP.*

By RICHARD EDWIN LEE, ROY H. UHLINGER, and FRANK O. AMON.

(Continued from p. 182).

PART II.—*Analysis of the Group*: (a). *General Discussion*; (b). *Test Experiments*; (c) *Adopted Procedure*; *Notes*.

(a) *General Discussion*.—In nearly all the schemes of qualitative analysis known to the authors the group precipitate is treated first with dilute hydrochloric acid in the effort to separate the readily soluble zinc and manganese sulphides from the more difficultly soluble sulphides of nickel and cobalt. Although this method is in very general use, the experiments conducted in this laboratory indicate that it does not meet the requirements of an accurate system of qualitative analysis. That others have experienced difficulties in endeavouring to make the separation is evidenced by the fact that the strength of the hydrochloric acid to be used in making the separation, as recommended by various authors, ranges from 0·5N to 5N. (Dennis and Whittlesey recommend 1N HCl; W. C. Morgan recommends 1N HCl; J. Stieglitz recommends 1N HCl (approx.); A. A. Noyes recommends 2N HCl; O. F. Tower recommends 2N HCl; J. H. Long recommends 2N HCl; F. M. Perkin recommends 2N HCl; F. P. Treadwell recommends 2·5N HCl; W. Böttger recommends 0·5N HCl; W. Segerblom recommends 5N HCl. Gooch and Walker separate Mn from Zn, Co, and Ni by the use of $HC_2H_3O_2$.) Our experiments, as well as those of others (Hertz, *Zeit. Anorg. Chem.*), 1901, xxvii., 390; 1901, xxviii., 343), have shown that the sulphides of nickel and cobalt are moderately soluble in 1N HCl, and that the presence of nickel and cobalt in the filtrate seriously interferes with the tests for zinc and manganese; if a weaker acid is used then the zinc frequently escapes detection by remaining in the residue, for it is known that zinc sulphide in the presence of nickel or manganese sulphide is not readily soluble in 0·1N HCl. Again, there is evidence at hand which indicates that the rate at which different sulphides dissolve in an acid of given strength is variable, and depends apparently upon the state of aggregation. In view of these difficulties, this method has been abandoned, and instead, all the sulphides are brought into solution by the use of hydrochloric acid and (solid) potassium chlorate.

The next step in the proposed method of analysis is the separation of zinc from manganese, nickel, and cobalt by the addition of sodium hydroxide and sodium peroxide. One of the main problems of this investigation was the determination of conditions which would insure an accurate separation of zinc. It is believed that the method as worked out and described in this paper has not been applied by any other author. By the treatment just mentioned, the manganese, nickel, and cobalt are completely precipitated as hydroxides of these metals in the trivalent condition and the zinc remains in the solution as sodium zincate. In this separation, advantage is taken of the fact which seems to have been overlooked by the majority of authors, namely, that cobaltic hydroxide, $Co(OH)_3$, is much less soluble than cobaltous hydroxide, $Co(OH)_2$, in an excess of sodium hydroxide. The zinc is precipitated and confirmed by conventional processes.

The separation of the hydroxides of manganese, nickel, and cobalt presented one of the most difficult problems connected with this investigation. The reaction finally selected for the purpose of separating manganese from nickel and cobalt is known as "Ford's Reaction." This reaction is frequently employed in iron and steel analysis, and consists in the conversion of the manganese into manganese dioxide by the action of chloric acid in the presence of strong nitric acid. The method of separating the manganese consists in dissolving the three hydroxides in strong hydrochloric acid, evaporating to a small bulk with an excess of nitric acid (1·20), adding (solid) potassium chlorate, boiling, and finally filtering off the manganese dioxide on a glass-wool-asbestos filter. This method has an advantage over the usual colour tests for manganese, in that an idea of the quantity of the element present may be obtained. Although a confirmatory test is unnecessary, the usual colour tests have been worked out and fitted to the system. Objections may be offered to this method, as it involves the use of an asbestos filter. When the operation (see Procedure IV., Note 2) has been executed once the objections will, in all probability, be withdrawn.

The filtrate (from the chloric acid precipitate) containing the nickel and cobalt is evaporated to expel the excess of acid and then made neutral with sodium hydroxide. T solution is divided into two parts and a test is made f each metal in the presence of the other; the nickel is pr cipitated by the use of potassium cyanide, sodium hy droxide, and bromine water as nickelic hydroxide; anc the cobalt as potassium cobaltic nitrite by the use of aceti acid and potassium nitrite. Provision is made for th usual borax-bead tests.

(b) *Test Experiments and References.* Series III.—Solubility of the Sulphides of Zinc, Manganese, Nickel, and Cobalt in Hydrochloric Acid.

0·2 grm. of Mn and 0·2 grm. of Zn as sulphides were precipitated from a cold ammoniacal solution and then digested with 25 cc. of 1N HCl; after 5 minutes treatment the sulphides were completely dissolved.

0·2 grm. of Ni and 0·2 grm. of Co as sulphides were precipitated from a cold ammoniacal solution and then digested with 25 cc. of 1N HCl; after 10 minutes treatment the mixture was filtered and the filtrate tested for N and Co by adding NH_4OH and H_2S. A heavy blac precipitate appeared at once. Approximately 0·04 grm of Ni and Co had dissolved.

This series of experiments shows that sulphides of nick and cobalt are moderately soluble in 1N HCl. Therefo zinc and manganese cannot be completely separated fro nickel and cobalt by the use of this reagent.

Series IV.—Action of Hydrochloric Acid on Various Mixtures of the Sulphides of the Group.

0·2 grm. of Ni and 0·0005 grm. of Zn as sulphides were treated with 25 cc. of 1N HCl; after ten minutes treatment the mixture was filtered and the filtrate tested for Zn by adding NH_4OH and H_2S. A heavy, black precipitate appeared at once, indicating that the NiS had dissolved. The *white* sulphide of zinc escaped detection, owing to the presence of a large mass of *black* nickel sulphide. Similar results were obtained when the experiment was

* *Journal of the American Chemical Society*, xxxv., No. 5.

repeated with quantities of Zn as ZnS varying in amount from 0·001 grm. to 0·02 grm.

These experiments show that a quantity of Zn as large as 0·02 grm. escaped detection, owing to the presence the Ni dissolved by the 1N HCl.

0·2 grm. of Zn and 0·0002 grm. of Ni as sulphides were treated with 25 cc. of 1N HCl; after 10 minutes treatment the sulphides were completely dissolved. This experiment was repeated with quantities of Ni varying in amount from 0·0003 grm. to 0·001 grm. Quantities of Ni smaller than than 0·0005 grm. were completely dissolved; on the other hand, it was found that ZnS in the presence of NiS was not completely dissolved in 1N HCl. Owing to these facts small amounts of Zn in the presence of relatively large amounts of Ni escaped detection.

Series V.—Action of Hydrochloric Acid and Potassium Chlorate on Mixtures of Sulphides.

0·2 grm. of Mn, 0·2 grm. of Zn, 0·2 grm. of Ni, and 0·2 grm. of Co as sulphides were treated with 25 cc. of HCl (1 : 12), and the mixture boiled for 5 minutes. A black residue proved to be a mixture of NiS and CoS. A few crystals of $KClO_3$ were added to the mixture. The residue dissolved at once.

Series VI.—Behaviour of Sodium Hydroxide and Sodium Peroxide towards Zinc, Manganese, and Nickel Hydroxides.

A solution containing 0·3 grm. of Zn as $ZnCl_2$ was made slightly alkaline with 5N NaOH. A white precipitate of $Zn(OH)_2$ appeared at once. The mixture was divided into two equal portions. When NaOH was added in moderate excess to one portion the $Zn(OH)_2$ dissolved, forming a clear solution of sodium zincate. A few grains of Na_2O_2 were added to the other portion—the $Zn(OH)_2$ was readily dissolved.

Similar results were obtained when the above experiments were repeated with hot solutions.

The composition of sodium zincate is probably not definitely known. Kunchert (*Zeit. Anorg. Chem.*, 1904, xli., 343—348) using Bodländer's electromotive-force method proved that solutions of sodium zincate contain chiefly ZnO_2-- and some $HZnO_2$-. Forster (*Zeit. Elecktrochem.*, 1899, vi., 301) has prepared solid $NaHZnO_2$. Hantzsch (*Zeit. Anorg. Chem.*, 1902, xxx., 298—303) from conductivity measurements, and Fisher and Hertz (*Zeit. Anorg. Chem.*, 1902, xxxi., 355) from dialysis experiments concluded that sodium zincate is almost completely hydrolysed into NaOH and $Zn(OH)_2$, and that the latter is present as a colloid.

0·2 grm. of Mn as $MnCl_2$ was completely precipitated by NaOH as flesh-coloured $Mn(OH)_2$, which turned brown owing to its oxidation (in the presence of air) to $MnO(OH)_2$. $Mn(OH)_2$ was found to be insoluble in excess of NaOH. $Mn(OH)_2$ is converted by Na_2O_2 into the brown hydrated MnO_2, probably $MnO(OH)_2$. The precipitation of Mn as $MnO(OH)_2$ by the use of NaOH and Na_2O_2 was complete.

From a solution containing 0·03 grm. of Ni as $NiCl_2$, NaOH, when added to alkaline reaction, completely precipitated the Ni as $Ni(OH)_2$. The precipitate was insoluble in excess of the precipitant. The precipitate was converted into black $Ni(OH)_3$ when treated with Na_2O_2. The filtrate gave negative results when tested for Ni.

Series VII.—Behaviour of Cobalt Salts towards Sodium Hydroxide and Sodium Peroxide.

0·03 grm. of Co as $Co(NO_3)_2$ was dissolved in 25 cc. of water and 2 cc. of HCl (1 : 12). The solution was made just alkaline with 5N NaOH, then 10 cc. *excess* were added and the mixture heated to boiling. The precipitate was filtered off, and the blue-coloured solution was acidified, then made just alkaline, and saturated with H_2S. A precipitate of CoS separated. This experiment was repeated, but 4 grms. of Na_2O_2 was added *before* the mixture was heated to boiling. The precipitate was converted into black $Co(OH)_3$, which was removed by filtration. The filtrate possessed a blue colour, which indicated that some of the cobalt had dissolved in the alkaline solution, forming a soluble salt, probably Na_2CoO_2, and when tested, as in the previous experiment, CoS separated.

0·03 grm. of Co as $Co(NO_3)_2$ was dissolved in 25 cc. of water and 2 cc. of HCl (1 : 12). The solution was made *slightly* alkaline with 5N NaOH. *No excess* of this reagent was added. 0·4 grm. of Na_2O_2 was added and the mixture heated to boiling. The dark coloured precipitate of $Co(OH)_3$ was filtered off; the filtrate was colourless and yielded no test for Co. This experiment was repeated many times with quantities of Co varying in amount from 0·0003 grm. to 0·5 grm.; in each experiment the precipitation was complete, the filtrate being colourless.

This series of experiments indicate that cobalt*ous* salts dissolve in excess of NaOH forming a blue solution; but if the cobaltous salts are first oxidised to the "-ic" condition by such agents as Na_2O_2 in NaOH solution, they are insoluble and therefore may be completely precipitated as $Co(OH)_3$. See Donath, *Zeit. Anal. Chem.*, 1901, xl., 137.

Series VIII.—Precipitation of Manganese Peroxide by Chloric and Nitric Acids.

See "Ford's Method," Olsen's "Quant. Chem. Anal.," p. 385, 3rd Rev. Ed., and Ford, *Trans. Am. Inst. Min. Eng.*, ix., 397 and 100. Experiments were conducted to prove that the presence of Ni and Co do not interfere with the reaction formulated as follows:—

$$KClO_3 + HNO_3 \longrightarrow HClO_3 + KNO_3$$
$$Mn(NO_3)_2 + 2HClO_3 \longrightarrow MnO_2 + 2HNO_3 + 2ClO_2.$$

Small pieces of filter-paper were placed in the casserole with MnO_2 and boiled with HNO_3 (1 : 20); all of the MnO_2 dissolved in 10 minutes. 0·0003 grm. of Mn as $MnCl_2$ in 25 cc. of water yielded a comparatively voluminous precipitate.

Series IX.—Confirmatory Colour Test for Manganese.

Following the directions outlined in Procedure IV., it was found that 0·0002 grm. of Mn could be easily detected. The violet colour due to the presence of the MnO_4 ion is very distinct.

$$2Mn(NO_3)_2 + 5PbO_2 + 6HNO_3 \longrightarrow 2HMnO_4 + 5Pb(NO_3)_2 + 2H_2O.$$

Series X.—Precipitation of Cobalt with Potassium Nitrite. Sensitiveness of Test.

0·0003 grm. of Co as $CoCl_2$ was treated according to Procedure VII.; the solution became turbid in 15 minutes. The experiment was repeated, using Ni instead of Co; the solution remained clear.

The above experiments were repeated, using 0·5 grm. of Co, and 0·5 grm. of Ni; results were the same.

See Procedure VII. and notes for further report.

Series XI.—Test for Nickel in Presence of Cobalt.

Following the directions given in Procedure VIII., 0·0003 grm. of Ni as $NiCl_2$ could be detected. A black precipitate, $Ni(OH)_3$ was obtained.

The experiment was repeated, except that 0·3 grm. of Co as $Co(NO_3)_2$ was used; no precipitate was observed.

Series XII.—Relative to the Accuracy and General Utility of the Proposed Method.

More than 100 students doing work in this laboratory in Qualitative Analysis during the past two years have used the methods proposed in this paper, and apparently have encountered no difficulties in following the procedures. Unknown mixtures particularly difficult of analysis have been given to the students in order to test the accuracy and utility of the methods. The instructor in charge of the work reports an unusually small percentage of failures. This is probably due to the fact that a moderate change in the conditions of precipitation does not greatly alter the accuracy of the methods.

(To be continued).

THE SCIENTIFIC WEEK.
(From Our Own Paris Correspondent).

Orchids and the Evolution of the Species.

For the last fifteen years a learned Frenchman, M. Noel Bernard, has been constantly studying the problem of the evolution of species that was, at one time, considered by many as inaccessible to laboratory methods, and reserved merely for the speculations of philosophers. By applying the Pasteurism methods to the study of the parasites of plants, M. Noel Bernard has, by decisive experiments, shown the preponderating *rôle* that have in all probability been played by microbian maladies in past millenniums in the evolution of vegetable species. This botanist has shown how one of the strangest flowers of our gardens, the orchid, cannot propagate unless the tiny seeds that fill the cavity of its fruit with an impalpable dust are attacked by parasitical fungi. The rudimentary seeds of the orchid are incapable of developing in the same conditions which suffice for the germination of other grains. M. Noel Bernard has reproduced in his laboratory diverse orchids. He has observed that living together with the fungi is imposed as a necessity to these perversely coloured flowers. Like Pasteur, Chamberland, and Roux, who showed that the virulence of bacteria can be increased, M. Noel Barnard has discovered a striking analogy of these phenomena in the case of orchids. By appropriate cultures the learned botanist has obtained far more active fungi than those that are normally met with, and capable of germinating a greater number of seeds of one seedling. From a general inquiry made concerning the parasitism of the higher grades of plants, MM. Noel Bernard, J. Magrose, and C. Bean have arrived at the conclusion that it is highly probable some state of vegetables must be considered as being, to a certain extent, the symptom of an infectious disease. Prof. Gaston Bonnier, in a notice that he read before the Academy in the name of M. C. Bean, has confirmed these researches. An orchid of our countries, the autumn spiranthis, has been the object of his studies. The germination of this orchid likewise cannot take place unless associated with a special filamentous fungi—the orchid gets rid of its associate to live separately. These experiments, which may find practical important application for the culture of all kinds of orchids, are susceptible one day of making biologists masters of the evolution of vegetable species.

Clouds and Terrestrial Magnetism.

An entirely new theory concerning clouds, advanced a few months ago by M. Birkeland, a learned Swedish physician, seems to be confirmed by a series of observations that an astronomer of the Lyons Observatory, M. Flajolet, has lately made on the *cirri*. These high clouds, that float at more than 9000 metres high, appear like parallel filaments, or turned over in the form of curls of hair. They often produce halos, and their apparition appears to be related to the variations of terrestrial magnetism. This concordance comes to support the hypothesis of M. Birkeland.

The Fluvial and Glacial History of the Rhone.

Few valleys have been the subject of more studies than the Valley of the Rhone in the neighbourhood of Lyons. Falsan and Chantre sought for the limits of the Rhodanian glacier in 1877. Recent researches have just been made by M. Ch. Duperet on the history of the Rhone in the Lyons region. They have been communicated to the Academy of Sciences by M. Douville. M. Duperet distinguishes two principal epochs, the period of pliocene alluviums, then that of quaternary alluviums. In the first, three terraces were formed, one 215 metres high; the second, from 140 to 145 metres high; the third, from 120 to 125 metres, this last against the Dombes. At the period of quaternary alluviums, M. C. Duperet has recognised a high terrace of from 90 to 95 metres that has been ravined to the bottom of the present valleys by the Rissien glacier. The Rhone glacier invaded the Lyonese region at the end of the quaternary period, consequently at a relatively recent epoch.

Plants Cultivated at the Neolithic Epoch.

It is generally admitted that the men of the age of hewn stone were exclusively hunters. With the invasions, probably of Asiatic origin, which brought into Europe a part of the Neolithics (dolichocephalic races) the manner of living changes; from pastoral it becomes sedentary. The Neolithics begin to raise domestic animals and to cultivate certain species of plants, the remains of which are to be found in the lake dwellings. Prof. Schenk has brought this question to an interesting point. Corn is the most ancient, or one of the most ancient, plants known. Prette and Boule have observed samples of it in the celebrated layer of the Mas d'Azil (Tourassian period or end of the hewn stone period). Corn is to be found in all the lake dwellings. It is identical to the Mottu corn still grown to-day (for straw for plaiting) in the Gruyère Valley, Canton of Fribourg. Zaborowski believes that this kind of plant is essentially of Asiatic origin. It would then have been brought into Europe by the dolicocephalic neolithic invaders. Egyptian wheat has also been found in several lake dwellings. Barley is also pretty frequent; it is represented by six very distinct varieties. On the other hand, rye and oats were known but were very rare. Flax was represented by a different kind from the present species, and which is still living to-day in a wild state in the Mediterranean basin. The other plants of the lake dwellings were probably gathered in a wild state. It was especially fruits which were generally cut in quarters and dried, such as certain little species of apples and pears; among these latter the present Swiss species of *Achras* has been found. Most of the wild fruit was consumed more or less accidentally. As to the origin of these neolithic species it does not seem that this question has progressed much since Heer and Candolle.

Pure Oxygen for Blast Furnaces.

The factories of Ougree-Marihaye began some few months ago to experiment on the use of pure oxygen instead of air in blast furnaces. The oxygen is extracted from the air by means of the Claude apparatus, well known to our readers. This substitution presents a great number of advantages; with oxygen it becomes unnecessary to force the combustive gas into the apparatus, the escapement gases in these conditions giving a greater quantity of heat, transformable into a motive form. It must be added that the functioning of the oxygen apparatus frees great quantities of pure nitrogen that can be utilised, for example, to manufacture nitrogenous manures. The experiments that have been made up till now have shown that the employment of oxygen would increase the production of the blast furnace very considerably (12 per cent), at the same time economising 5 per cent of coal.

Intervention of the Number π in the Relations between Atomic Weights.—P. Dambier.—From the comparison of the atomic weights of certain elements it appears that these numbers depend upon one another by relations which involve the Number π (3·141593). The author has arrived at this result by investigating the eight elements Cl, Br, I; C, N, O, S, and H. The following are some of the values of π calculated by using the atomic weights of Guye:—

$$\frac{CN}{2CN - Cl} = \frac{\pi}{2} \qquad \pi = 3{\cdot}1415$$

$$\frac{HCl + 2\pi}{NH_3 - 2\pi} = 4 \qquad \pi = 3{\cdot}1416.$$

—*Journal de Chimie Physique*, xi., 2.

NOTICES OF BOOKS.

Chemistry and its Relations to Daily Life. By Louis Kahlenberg and Edwin B. Hart. New York: The Macmillan Company. 1913.

This book is intended to provide a year's course of theoretical and practical chemistry for students of agriculture and home economy in technical schools. The authors have endeavoured to give a thoroughly sound and scientific presentation of their subject, and have succeeded in producing a work which will be specially suitable for agricultural students, and will give them a good grounding in the application of the principles of chemistry to problems in farming. For a single year's work too wide a region is covered, and there is perhaps rather too much detail; for example, some of the more complicated formulæ might well be omitted. The short course of laboratory work is well-planned and useful, and the use of different kinds of type in the text and the constant emphasis laid on important points ought to make it very easy for the student to get a good grasp of the salient features of the chemistry of everyday life.

The Chemistry of Rubber. By B. D. Porritt, B.Sc. (Lond.), F.I.C. London: Gurney and Jackson. 1913.

In this monograph the properties, constitution, and vulcanisation of rubber are briefly treated from the chemical point of view. A certain amount of space is devoted to the consideration of some matters of technical importance, but usually only in so far as it is necessary to be acquainted with them in order to obtain a clear grasp of the chemical questions involved. The evidence which has been accumulated as to the constitution of caoutchouc is clearly and impartially put before the reader, and the recent work which has been done on the synthesis of rubber and the preparation of isoprene is described. The chemist who is specially interested in the rubber industry will find the full bibliography very useful and the monograph will serve as an admirable introduction to the detailed study of the copious literature on the subject.

The Work of the Dominion Experimental Farms. By Frank T. Shutt, M.A., F.I.C., F.R.S.C. Toronto: The University Press. 1913.

The address printed in this pamphlet was read before the Canadian Institute, Toronto, in December, 1912. It contains a short history of the establishment of the five original Dominion Experimental Farms in 1866, and of the experimental stations which are the offshoots of them, and gives some account of the work which has been done in the several departments of these farms and stations. The author has thought it necessary to recapitulate some rather elementary and, one would have thought, well-known facts, such as the need for keeping stock and for the rotation of crops, but on the other hand he has some interesting remarks to make upon the results which have been collected in the investigations of different varieties of cereals. He also touches upon the research work done in horticulture, botany, and poultry keeping, and his report shows that the farms are doing a very valuable work, which is thoroughly appreciated by the farmers of the Dominion.

Les Propriétés Optiques des Solutions. ("The Optical Properties of Solutions"). By C. Chéneveau. Paris: Gauthier Villars. 1913.

This book is practically a new edition of the author's thesis on the same subject which was published four years ago. As in the original only two optical properties, dispersion and refraction, are discussed, but a very comprehensive account is given of the work which has been done on them. Some facts and theories of historical interest only have been omitted, to make room for a full discussion of recent results, and the author shows good judgment in the choice of his material. Thus, while he includes a certain number of experimental results, for fuller data he refers his readers to Tables of Physical Constants, and throughout the whole book he emphasises general principles without going into minute details. The determination of the constitutional formulæ of organic substances from the study of their optical properties is treated very satisfactorily, and the different types of apparatus employed in measuring refraction and dispersion are well described.

The Year-Book of Wireless Telegraphy and Telephony. 1913. London: The St. Catherine Press.

This year-book is the first work of its kind to be issued to the public, and there can be no doubt but that the increasing number of people who are interested either commercially or scientifically in wireless telegraphy will find it very acceptable. The editor had no easy task in meeting the very different requirements of these two classes of readers, but on the whole he has apportioned out his space judiciously, and there will be but few alterations in that respect to make before the next edition is issued. The Laws and Regulations of all countries are printed in full, and a complete list of all the wireless telegraph stations of the world, with call signals and other particulars, is given. The articles contained in the book deal with Wireless Time Signals, The Wireless Direction Finder, The Technical Situation of Radiotelephony, Wireless Telegraphy for Military Purposes, The Principles of Wireless Telegraphy Explained by Mechanical Analogies, &c. A dictionary of technical terms in five languages is included, and a catalogue is given of Applications for Patents in 1911 and 1912. The yearly record of progress in wireless telegraphy, which opens with the year 1896 might well have been taken a few years further back so as to include the suggestions and experiments of the true pioneers in this region, who foresaw the practicability of the application of the Hertzian waves in telegraphy, and pointed out in the clearest language what experiments were necessary in order that the then apparently impossible feat of transmitting messages by telegraphy without wires might be accomplished.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Academie des Sciences. Vol. clvii., No. 3, July 21, 1913.

Action of Gaseous Hydrofluoric Acid on Quartz.—Armand Gautier and P. Clausmann.—The authors have found that hydrofluoric acid has hardly any action on the surface of quartz which is perpendicular to the axis, while the surface parallel to the axis is rapidly attacked. Similarly, the facets corresponding to the direct rhombohedron in a crystal are not attacked, while those corresponding to the inverse rhombohedron are etched, like the surface parallel to the axis. This is the first time it has been proved that there is a relation between the orientation of the different faces of a crystal, and hence the orientation of the molecules of which it is formed, and the energy of the chemical actions which the different facets undergo.

Tetra-alkylation of α- or 1-Methylcyclohexanone.—A. Haller.—The author has shown that the preparation of ethyl derivatives of cyclohexanone by means of sodamide gives very poor results, owing to the condensation of the ketone with itself. If, however, the fundamental ketone

ontains a methyl group the reaction becomes possible, and it occurs more easily the nearer the methyl is to the carbonyl group.

Composition of Essence of Coffee. Presence of Pyridine.—Gabriel Bertrand and G. Weisweiller.—Erdmann has found that an aqueous infusion of coffee contains traces of acetic acid and furfurol, appreciable amounts of valeric acid and furfuric alcohol, a nitrogenous substance having the smell of coffee, and a certain proportion of phenolic substances resembling creosote. The authors find the substances mentioned by Erdmann do not when mixed give the aroma of infusion of coffee, and there is in the aqueous liquid a basic substance, which can be separated by means of silicotungstic acid, and proved to be pyridine. The amount of pyridine present is greater than that of all the other substances put together.

Action of Water on Carbides of Rare Earths.—A. Damiens.—When water acts on the carbides of cerium, lanthanum, neodymium, praseodymium, samarium, the chief gaseous products are acetylenic hydrocarbons. In addition hydrogen, ethylene, propylene and its homologues, ethane, propane, and butane are formed. No methane is ever produced. The acetylenic hydrocarbons include acetylene, allylene, and the vapours of heavier hydrocarbons. The oxides obtained are always sesquioxide hydrates, and the action is $C_2M+3H_2O=M(OH)_3+C_2H_2+H_2$. The hydrogenation of acetylene gives ethylene and ethane.

Spontaneous Transformation of Hypochlorites into Chlorates and Hypobromites into Bromates.—J. Clarens.—When solutions of commercial hypochlorites are converted into chlorates no chlorite is formed. In solutions of hypobromites the presence of bromite can be detected before any bromate is formed. The following reaction first occurs:—$2KBrO=KBr+KBrO_2$. The bromite is then oxidised by the hypobromite as follows:—$KBrO+KBrO_2=KBr+KBrO_3$, or else it is transformed into bromate, thus, $3KBrO_2=2KBrO_3+KBr$.

Catalytic Preparation of Ketones by Oxides of Iron.—A. Mailhe.—The oxides of iron can conveniently be employed as catalysts to bring about the preparation of ketones from acids. Either ferrous oxide, obtained by heating oxalate of iron in a closed tube, or ferric oxide, obtained by the calcination of ferrous oxalate in air, can be employed. Ferric oxide is a particularly good catalyst. The worst yields are obtained with isovaleric and isobutyric acid. During the catalysis it is partially reduced to ferrous oxide, which itself possesses catalytic powers.

Action of Sodammonium on Phenylacetylene and on Styrolene.—Paul Lebeau and Marius Picon.—When phenylacetylene is hydrogenated with sodammonium the action does not stop at the corresponding ethylenic hydrocarbon, as in the case of the true acetylenic hydrocarbons of the fatty series, but the saturated hydrocarbon is also formed, namely, ethylbenzene. The intermediate ethylenic hydrocarbon, styrolene, is transformed into ethylbenzene by the sodammonium, with formation of sodamide.

Bulletin de la Société Chimique de France.
Vol. xiii.-xiv., No. 14, 1913.

Synthesis of Glucosides by means of Ferments.—Em. Bourquelot.—The author has shown that some ferments, *e.g.*, emulsin, are both hydrolysing and synthesising in their action, or, in other words, their action is reversible. There is a close resemblance between their action and the hydrolysis and formation of ethers. Thus, secondary alcohols more readily undergo both glucosidification and etherification than primary alcohols. The action is not limited only to those alcohols which are liquid at the temperature at which the ferments act. Certain organic compounds which are absolutely insoluble in water may, under the influence of ferments, form soluble compounds with glucose; this phenomenon is of great importance in biochemistry, for glucose is always present n living substances.

Determination of Copper by Methanal Sulphurous Acid.—Philippe Malvezin.—To prepare methanal sulphurous acid SO_2 is bubbled through a 40 per cent commercial solution of formol. The solution is standardised by titrating it with a solution containing 1 grm. of red copper in HNO_3, made up to 100 cc. To titrate, 1 cc. of this solution, 2 cc. of ammonia, and 1 cc. of distilled water are placed in a test-tube, and the acid is added from a burette until the deep blue coloration first becomes green and then the solution becomes colourless. This ought to take about 5 cc. of acid. To determine the copper in a substance about 0·1 grm. is gently heated, and the residue treated with HNO_3. The liquid is made up to 20 cc. with distilled water. Ten cc. are filtered off. Two cc. of ammonia are added, and the liquid is again made up to 20 cc. with distilled water, and filtered. Ten cc. of the new filtrate are taken for the titration, 1 cc. of ammonia being added. If n is the number of cc. used in the titration with the known copper solution $x=\frac{40\times n'}{n}$, where n' = the number of cc. of acid actually employed.

MISCELLANEOUS.

Chemical Society.—An Extra Meeting of the Chemical Society will be held at Burlington House, Piccadilly, W., on Thursday, October 23, 1913, at 8.30 p.m., when the Ladenburg Memorial Lecture will be delivered by Prof. F. Stanley Kipping, D.Sc., F.R.S.

Institute of Chemistry.—Mr. W. P. Dreaper, F.I.C., will deliver the first of two lectures on "The Research Chemist in the Works, with special reference to the Textile Industry," on Wednesday, October 29th, 1913, at 8 p.m., at the Imperial College of Science and Technology, South Kensington, London, S.W.; Prof. Raphael Meldola, D.Sc., F.R.S., President, in the Chair. *Syllabus of Lectures*:—The British Textile Industry. Nature of training required for textile research. Conditions which govern investigation. Interpretation of results. Time and cost factors. Secret working. Improvements in plant and manufacturing operations. Originality an essential factor. Influence of local conditions on industry. Works research laboratory. Establishing experimental works. Nature of investigation. Study of detail a key to success. Mercerising and Schreinering. Value of observation. The chemist and the workman. Technology of textile fibres: Methods of manufacturing artificially prepared yarns and fabrics; their value in commerce; introduction of new fibres; variations in raw materials. Influence of theory. Is the action of dyeing, physical, electrical, or chemical? Chemical constitution and physical properties of fibres. "Neutral salt" reactions in presence of fibres, &c. Bleaching, dyeing, printing, and finishing operations. New dye-stuffs and their application. Silk weighting. Types of machinery used. Water supply. Special processes: Embossing, waterproofing, and gas-proofing fabrics; "cross-dyeing" effects; dyeing furs; action of heat and moisture, &c. The chemist and engineer. New processes and management of plant. Electro-bleaching. Electro-typing. Use of spray. Disposal of waste liquors. Development of textile research, and its systematic treatment.

MEETINGS FOR THE WEEK.

TUESDAY, 21st.—Royal Photographic Society, 8. "Photomicrography and Jam Adulteration," by E. Marriage.
THURSDAY, 23rd.—Chadwick Public Lectures, 5. (The University, Bristol). "Physiological Principles of Heating and Ventilating," by Dr. Leonard Hill.
— Chemical, 8.30. The Ladenburg Memorial Lecture will be delivered by Prof. F. S. Kipping, F.R.S.
FRIDAY, 24th.—Physical, 5. "The Ice Calorimeter," by E. Griffiths. "An Electrostatic Oscillograph," by H. Ho and S. Kotò.

THE CHEMICAL NEWS.

VOL. CVIII., No. 2813.

THE SOLIDIFYING- AND MELTING-POINTS OF MIXTURES OF STEARIC AND OLEIC ACIDS.

By ROBERT MELDRUM

THE following investigation was undertaken to confirm the degree of accuracy of Dalican's method of determining the solidifying-point and the thermometer bulb method of determining the melting-point of mixtures of fatty acids. As the same thermometer was used throughout, the investigation was a very prolonged and tedious one. As the readings and observations were made with great care, that is the main apology for their publication.

The solidifying-point and melting-point is the only means available of determining the degree of purity of innumerable organic compounds, and is also of importance in the examination of mixtures of fatty acids and organic mixtures having well-defined solidifying- and melting-points. The use of the solidifying- and melting-point methods may be further extended in analytical work by melting down 50 per cent of the sample with 50 per cent of some suitable non-volatile solvent such as aniline, oleic acid, sperm oil, or mineral oil, and determining the melting-point or solidifying-point at such dilution. But before such methods as these can be applied to comparative analysis it is necessary to know the limit of accuracy inherent in the methods of solidifying- and melting-point determinations in some standard mixtures, and that is the reason why stearic and oleic acids were selected for this work.

The solidifying-points were taken in a test-tube 7 inches by 1 inch, filled three parts full. Tubes of greater diameter have greater advantages over narrower tubes, as the cooling is slower, and there is more matter between the thermometer and walls of tube. The test-tube was passed through a bung fixed to glass jar. The thermometer used was a 60° C. divided into one-tenths. The mixtures were melted and cooled to 10° C. above their solidifying-point fixed in jar, and when crystallisation had commenced at bottom the whole was very slowly stirred till the thermometer ceased to fall, then thermometer was fixed in centre 1½ inches from bottom and the readings completed. The point at which the thermometer rose and remained stationary was called the solidifying-point. Five determinations were made of each mixture, the results being recorded below. The oleic acid used had solidifying-point 8° C., the stearic acid 54.8° C.

Solidifying-point by Constant Stirring Method.

Oleic acid. Per cent.	Stearic acid. Per cent.	Solidifying-point +rise °C. Min.	Max	Avg.	Rise °C. Min.	Max.	Avg.	Difference in solidifying-point for each increment of 10 per cent oleic (°C.).
0	100	54.6	54.9	54.8	0.7	1.1	0.8	—
10	90	53.2	53.4	53.3	0.8	0.9	0.8	1.5
20	80	51.6	51.6	51.6	0.9	1.0	0.9	1.7
30	70	49.6	49.8	49.7	0.9	1.0	1.0	1.9
40	60	47.4	47.6	47.6	1.0	1.2	1.1	2.1
50	50	44.6	44.8	44.7	0.9	1.2	1.0	2.9
60	40	41.1	41.3	41.2	1.0	1.1	1.0	3.5
70	30	34.6	36.7	36.6	0.4	0.9	0.6	4.6
80	20	30.3	31.0	30.5	0.7	0.5	0.5	6.1

It will be seen from above that this method of constant stirring yields very concordant results for any given mixture; the maximum difference being 0.3° C. up to 70 per cent oleic, and increasing to 0.7° C. at 80 per cent. But this greater error is overbalanced by the greater difference in solidifying-point between 70 and 80 per cent oleic, which is 6.1° C. It is generally accepted that the accuracy of the solidifying-point decreases in proportion to its decrease; and this is the reason why the titre is seldom applied to low melting mixtures, as the determinations are treated as unreliable. But when we examine this point more closely we see that such is not the case, and, on the contrary, the low melting mixtures yield results more constant in accuracy than the high melts, as the following figures will show.

Difference in Solidifying-point for each Increment of 10 per cent Oleic (°C.).

A.	1.5	1.7	1.9	2.1	2.9	3.5	4.6	6.1
	Limit of Accuracy (°C.).							
B.	0.2	0.0	0.2	0.2	0.2	0.2	0.1	0.7
	Percentage B *on* A (°C.).							
	13.3	0.0	10.5	9.5	6.9	5.7	2.1	11.4

These figures clearly show that with stearic acid the determination is only accurate to within 13.3 per cent, and with the 80 per cent mixture the accuracy is 11.4 per cent. But the important fact here brought out is that the error of accuracy decreases with a decrease in the solidifying-point. In other words, the softer mixtures give more reliable results. It will be observed that 10 per cent oleic acid only lowers the solidifying-point by 1.5° C., or 1 per cent = 0.15°, which is beyond the limit of accuracy of the test; 2 per cent oleic acid would only lower the solidifying-point by 0.30° C., the actual limit of accuracy. Whereas with the 80 per cent mixture a difference of 1 per cent oleic would affect the solidifying-point by 0.61° C., nearly the actual accuracy at that dilution. With the 70 per cent mixture each per cent oleic present = 0.46° C. It is therefore evident the more accurate the determination the lower the solidifying-point. That is why in two given samples, of the same solidifying-point, when melted down in some solvent and the solidifying-points determined, a difference at these dilutions will often be found between them.

With all solidifying-point determinations the number of degrees the thermometer rises and remains stationary are very important points, which will often yield to the analyst information not otherwise available. So far as these mixtures are concerned the maximum rise remains constant at between 30 and 60 per cent oleic acid. As the solidifying-point falls the "rise" increases, then remains constant, and again falls.

Another series of solidifications were made under the same conditions and the same apparatus and the same mixtures but *without* stirring, the thermometer remaining stationary all the time. The following are the results:—

Solidifying-point by Stationary Method.

Oleic acid. Per cent.	Stearic acid. Per cent.	Solidifying-point +rise. Min.	Max.	Avg.	Rise °C. Min.	Max.	Avg.	Difference in solidifying-point for each increment of 10 per cent. oleic.
0	100	53.6	53.9	53.7	0.2	0.3	0.3	—
10	90	52.2	52.4	52.3	0.3	0.5	0.4	1.4
20	80	50.8	50.9	50.9	0.7	0.8	0.7	1.4
30	70	48.9	49.0	49.0	0.7	1.0	0.8	1.9
40	60	46.4	46.6	46.6	0.5	0.9	0.7	2.4
50	50	43.6	43.7	43.6	0.7	0.8	0.8	3.0
60	40	39.8	40.1	39.9	0.5	0.1	0.7	3.7
70	30	35.3	35.6	35.4	0.4	0.6	0.5	4.5
80	20	29.2	29.4	29.2	0.3	0.6	0.4	6.2

By this method the readings agree within themselves by 0.3° C., the limits of accuracy, and confirm in all detail the results obtained by the first method. There are, however, two distinct differences between the methods. By the

stirring method the rise is higher and the solidifying-points are also higher, as will be seen from below :—

Average Rise in T° by both Methods.

Oleic. Per cent.	Stirring. °C.	Stationary. °C.
0	0·8	0·3
10	0·8	0·4
20	0·9	0·7
30	1·0	0·8
40	1·1	0·7
50	1·0	0·8
60	1·0	0·7
70	0·60	0·5
80	0·5	0·4

Here it is clear the quicker the cooling the higher the rise. The rise is apparently governed by the amount of matter crystallised per interval of time. With solidifying-point determinations it is the usual custom to include the "rise" in the solidifying-point, as the solidifying point is the highest temperature at which solidification takes place, and is well-defined, due to the thermometer remaining stationary for long periods at that point. Thus,—

Per cent oleic acid	0	10	20	30
Minutes thermometer remains stationary	30	20	12	12

But then, again, the lowest temperature to which a liquid must be cooled to produce a homogeneous solid may also be stated to be the true solidifying-point. The most troublesome part of the "rise" is that it is far from constant, varying in any series as much as 0·5° C. But most likely this is due to the commencement of the rise not being well-defined and erratic. This point requires further investigation as it is of some importance. Where the solidifying-point of a substance having no "rise" requires to be compared with another having a "rise" of 1° or 2° C. the comparison is very troublesome and confusing. But "rise" or no "rise" the point is well-defined in both cases where the thermometer remains for the longest period stationary. Some stearic acid was melted in test-tube and this plunged in cold water; the solidifying-point indicated was 53·9° C. with a rise of 0·3° C. In another experiment 200 grms. of a 10 per cent oleic acid and 90 per cent stearic acid were placed in glass ball, the thermometer placed in centre and allowed to cool. The T° fell to 51·8° C, and remained for over 30 minutes at that without showing a "rise." This only indicates the troublesome nature of the "rise" which depends on thermal conditions, which may or may not be present at any given time. The rise is apparently eliminated when working with large quantities, due to the slow rate of cooling. It seems to me the direction in which the "rise" is likely to be eliminated from the test is by conducting the solidification in a hot water jacket. It will be apparent that to eliminate the "rise" would not affect the longest interval at which the thermometer remains stationary, but would lower all the readings.

Of the two methods the stationary method yields the lower results uniformly through the whole series as follows :—

Oleic. Per cent.	Stirring. °C.	Stationary. °C.	Difference. °C.
0	54·8	53·7	1·1
10	53·3	52·3	1·0
20	51·6	50·9	0·7
30	49·7	49·0	0·7
40	47·6	46·6	1·0
50	44·7	43·6	1·1
60	41·2	39·9	1·3
70	36·6	35·4	1·2
80	30·5	29·2	1·3

This difference is not due entirely to the difference in "rise," but most likely is due to rapidity of crystallisation. The methods show, with stearic acid alone, a difference of 1·1° C., which is equivalent to about 7 per cent oleic acid. The question is which method approximates the true solidifying point, and from our foregoing argument there can be no hesitation in determining that to be the stationary method.

The relationship between the solidifying point and melting point is generally somewhat obscure, the general idea being that the melting-point is always higher than the solidifying-point. The author's experience extending over the past twenty years confirms that, working with a varied assortment of substances and various melting-point methods. But it would appear that the ratio between the melting-point and solidifying-point depends on the melting-point method used, there being no definition of what the actual melting-point really is. A series of determinations were made of the melting-point by the thermometer bulb method, using the same thermometer and the same mixtures of stearic and oleic acid as used for determining the solidifying-point. The thermometer was dipped into the melted fat at about 10° C. above its melting-point; and with the low melting mixings the thermometer was cooled down to 0° C. before dipping to obtain a uniform coating throughout the series. The thermometer was fixed in test-tube $\frac{3}{4}'' \times 7''$, fixed in beaker of water, and heated gradually while stirring the water. So far as these mixtures are concerned, cooling the thermometer down for twenty-four hours after coating with fat and thirty minutes cooling, no difference was found in melting-point. Cooling down quickly at 0° C. and at 15° C. no difference in melting-point was observed. Numerous observers have frequently pointed out the importance of prolonged cooling, and have obtained differences in the melting-point of several degrees when rapidly cooled. So far as this method is concerned, constant results depend not on the rate of cooling but on the uniform coating of the thermometer bulb. If the coating is too thin the melting-point is likely to be high, due to the fact that the temperature of fat must be increased above its actual melting-point to produce sufficient viscosity to cause it to flow into a bead. On the other hand, when the film is too thick the fat begins to flow and forms beads below its melting-point, as numerous, if not all, solids flow below their melting-point, but in all these cases opacity is present. The following determinations were made with the greatest possible care, five being made for each series :—

Melting-point by Thermometer Bulb Method of Mixtures of Stearic and Oleic Acids.

Oleic acid Per cent.	Stearic acid Per cent.	Melting-point °C. Minimum.	Maximum.	Average.	Difference for each 10 per cent oleic.
0	0	55·4	55·8	55·6	—
10	90	53·8	54·0	54·0	1·6
20	80	52·1	52·6	52·3	1·7
30	70	49·8	50·4	50·1	2·2
40	60	47·5	47·8	47·6	2·5
50	50	45·2	45·3	45·3	2·3
60	40	42·0	42·5	42·3	3·0
70	30	37·8	38·2	38·1	4·2
80	20	32·8	33·4	33·0	5·1

This method it will be seen is only accurate within 0·5° C. for all the series. The following shows the difference between the melting-point and solidifying-point by stationary method :—

Per cent.	Melting-point. °C.	Solidifying-point. °C.	Difference. °C.
0	55·6	53·7	1·9
10	54·0	52·3	1·7
20	52·3	50·9	1·4
30	50·1	49·0	1·1
40	47·6	46·6	1·0
50	45·3	43·6	1·7
60	42·3	39·9	2·4
70	38·1	35·4	2·7
80	33·0	29·2	3·8

The curious fact is that there is a decrease in difference between the melting-point and solidifying-point from 0° to 40 per cent, and then an increasing difference for the remainder of the series. The melting-points approximate more closely to the solidifying points by the stirring method as follows:—

Oleic. Per cent.	Melting-point. °C.	Solidifying-point. °C.	Difference. °C.
0	55·6	54·8	0·8
10	54·0	53·3	0·7
20	52·3	51·6	0·7
30	50·1	49·7	0·4
40	47·6	47·6	0·0
50	45·3	44·7	0·6
60	42·3	41·2	1·1
70	38·1	36·6	1·5
80	33·0	30·5	2·5

The differences here are lower than by the stationary method. At the 40 per cent mixture the difference is least, being equal to each other. The melting-point of the 10 per cent mixture was determined by the capillary tube method, which yielded readings as follows:—52·6, 51·8, 52·4, 52·2; average = 52·2° C. Here it will be noted the melting-point is lower than the solidifying-point by either method, and nearly 2° lower than the melting-point method by thermometer bulb.

The melting-point of stearic acid was determined by a new method not hitherto published. U-tubes with 12 cm. legs by 2·5 mm. bore by 1 mm. thick were used. The stearic acid was melted and sucked into leg, and when cold end of U-tube was heated to melt out 6 cm. of the fat, leaving a column of 4 cm. in leg. The thermometer was placed between legs, and the U-tube immersed in water and heated at rate of 0·5° C. per minute while stirring. The temperature at which both columns of fat are of equal height is the melting-point. The figures obtained were:—55·4, 55·4, 55·5, 54·6, 55° C.; limit of accuracy, 0·9° C. The fat remains opaque even when maintained at a temperature of 56° C. for thirty minutes, and only clarifies when heated to 57·8° C. The inherent weakness of this process is that the fat flows while still opaque. Another method was tried by using straight tubes 12 cm. long by 2·5 mm. bore by 1 mm. thick. In this case the tube is dipped into melted fat to the extent of 4 cm., finger placed on top and removed, and allowed to cool. This tube is now fixed to thermometer with india-rubber band and placed in beaker of water heated at rate of 0·5° C. per minute while stirring, the water level being 4 cm. above fat. The temperature at which the column ascends is the melting-point. This method gave:—53·8, 53·8, 54·4, 53·8, 53·8, 54·0, 54·4° C.; limit of accuracy, 0·7° C. The defect of this method is that the column of fat commences to ascend while still solid and opaque, due to the fact that the core of fat becomes fluid on outside, leaving a solid core inside. Another objection is that the movement of the fat depends on pressure. The process, however, yields very constant results. The ordinary capillary tube method gave:—54·8, 55·4, 55·6, 55·2; error of accuracy, 0·8° C.

The following is a summary of these melting-point determinations:—

	Min.	Max.	Avg.	Limit of accuracy.
Thermometer bulb	55·4	55·8	55·6	0·4° C.
U-tube	54·6	55·5	55·2	0·9° C.
Straight tube ..	53·8	54·5	54·1	0·7° C.
Capillary tube ..	54·8	55·6	55·2	0·8° C.

According to these determinations the bulb method is the most accurate, yielding the most constant results with least variation. By the four methods the melting-point is in each case higher than the solidifying-point, and as is well known the melting-point varies according to the method used. It therefore would appear that the melting-point is only apparently higher than the solidifying-point, due to all melting-point methods yielding too high results.

PRODUCTION OF HYDROCARBONS FROM A SOLUTION OF SODIUM STEARATE BY ELECTROLYSIS.

By H. T. F. RHODES.

As is well known, it is possible to produce ethane by the electrolytic dissociation of potassium acetate—

$$\begin{array}{llll} CH_3 & COO & K + HO & H \\ + & & & - \\ CH_3 & COO & K + HO & H \end{array}$$

As the number of carbon atoms rise dissociation by electrolysis becomes more difficult. Probably the cause of this in the case of sodium stearate, and the salts allied to it, is the partial hydrolysis which takes place when these salts are dissolved in water. It has been found possible, however, by using a very low current, to dissociate an aqueous solution of sodium stearate.

Three grms. of pure hard soap, consisting entirely of sodium stearate, were dissolved in 100 cc. of water. The solution was acified with acetic acid, and electrolysed for fourteen hours, using 0·3 ampère. The solution was then diluted with water, and was allowed to stand for a week; it was then filtered, and a small quantity of a hydrocarbon very similar in physical properties to paraffin wax was obtained. It is interesting to note that the hydrocarbon could not be detected in the solution until it had stood for some considerable time. It was probably in a very fine state of division immediately after electrolysis.

The data is not very satisfactory, as reliable results were obtained on two occasions only, and in each case the yield was so small that it was impossible to definitely decide its exact composition.

NEW RESEARCHES ON LIQUID CRYSTALS.*

By O. LEHMANN.

(Continued from p. 182).

II. *The Objections Urged against the Existence of Liquid Crystals.*

HERR MLODZIEJOWSKI, who disputes the existence of liquid crystals (*loc. cit.*), did not perform the experiments described above. He merely allowed the solution (containing excess of water) obtained by his method to evaporate under the microscope, when naturally the composition of the solution was continually changing and important complications must arise at the free surfaces owing to the effect of surface tension.

From similar observations of *uncovered* solutions, M. Vogelsang ("Die Kristalliten," Bonn, 1875) had already arrived at the erroneous conception of the existence of attraction forces of crystals by means of which they can influence other crystals which are free to move, just as magnets can attract and arrange other magnets. For the same reason Herr M. had no difficulty in explaining by means of hypothetical forces the anisotropism and clustered formation of the structures observed by him, as well as the phenomenon of again assuming their normal structure when they flow together; these forces are supposed to be exerted upon one another by invisibly small solid crystals of anhydrous ammonium oleate when they are suspended in oleic acid. But such mysterious actions at a distance between crystals are unknown in physics; even with crystals molecular forces act only at molecular distances.

According to G. Quincke (*Wied. Ann.*, 1894, liii., 615), who is the originator of this theory after Herr M., the directive forces which the crystals experience proceed from the surface skin of the oleic acid. These influence soap

* Abridged from *Sitzungsberichte der Heidelberger Akademie der Wissenschaftung*, 1913, A, xiii.

crystals just as a thin layer of mica affects little crystals of potassium iodide, and forces them to arrange themselves in definite positions. But only the hypothetical layer of invisible tiny crystals lying close to the surface could be thus arranged, and the arrangement would not be that which is actually observed. For with simple liquid crystals the extinction between crossed Nicols is absolute; the molecular axes can thus form all possible angles with the surface, whereas they should be perpendicular to it. Herr M.'s hypothesis moreover provides no explanation of the fact that the smallest simple crystals always exhibit the form of an extended tetragonal octahedron or its growing form (more projecting edges), and thus possess an axis of symmetry of the second order (except in the case of the rounding of the surface, which is also to be seen in many soft solid crystals of simple structure, like ammonium chloride, silver iodide, camphor, &c.). What force could then produce four projections (90° apart) in the drops of oleic acid drawn out longways into the shape of a spindle (by some inexplicable force), and moreover always four projections and never one or two or three? This phenomenon can only be explained on the assumption that the smallest crystals, which have been undisturbed during growth, have a lattice structure like solid crystals.

The disappearance of the parallelism of the secondary axes when the crystals flow together is due to the fact that, as the phenomenon of forced homotropism shows, the molecules can turn very easily about the principal axis (optical axis). The molecules must be regarded as leaflets which endeavour to become parallel when the crystals flow together, but remain irregularly arranged as regards the direction of the secondary axes, so that the resulting semi-isotropic structure possesses an unlimited number of planes of symmetry through the principal axis. Of the eight projections which two crystals flowing together possess, two could easily disappear, so that only six remain, which at once arrange themselves symmetrically. They no longer correspond to a lattice structure, but produce disturbances of the semi-isotropic structure. From the flowing together of more crystals, structures with 10, 14, or more projections could result. This fact is in good agreement with the theory of liquid crystals.

Another mystery, the explanation of which Herr M. leaves to the reader, is the fact that the hypothetical crystals of anhydrous ammonium oleate suspended in the drops of oleic acid have such minute dimensions that they are invisible even when magnified by the strongest microscope, while this salt when it crystallises from oleic acid appears as distinct crystals which can easily be recognised when slightly magnified. This mystery will never be explained, for owing to the large amount of water in Mlodziejowski's preparation it has been proved above that crystals of anhydrous neutral ammonium oleate could not be formed in the drops of oleic acid. If there could be any question of solid crystals, they would be crystals of acid ammonium oleate hydrate, which, however, as has already been said, are very large. Even if we disregard this contradiction of experience we are at once confronted with a new mystery.

What explanation could be given of the fact that the drops of oleic acid remain unchanged in an aqueous solution saturated with ammonia? As has already been pointed out, an excess of ammonia is very favourable to the formation of liquid crystals, while lack of ammonia prevents their formation and converts all the crystals that have been formed and the oleic acid into solid acid ammonium oleate. Herr M.'s article provides no answer to these questions, which he naturally does not suggest, being ignorant of the facts. If Herr M. had tried to destroy the supposed drops of oleic acid, *i.e.*, the liquid crystals, by the addition of gaseous ammonia, he would have observed, in contradiction to his theory, that the liquid crystals were *not* destroyed, but that, on the other hand, they appeared more stable the greater the excess of ammonia.

Herr M. does not explain why the "chrysalis-like" structures of oleic acid and solid crystals of ammonium oleate look exactly like the liquid crystals of other chemically well-defined substances, in the case of which a decomposition into solid crystals and an oily isotropic liquid is precluded for chemical reasons. According to his observations the oleic acid can be pressed out of the liquid crystals, and often even flows out of them of its own accord in the form of a drop. Here, again, there is an error. For if the structures in which this was observed were actually those called liquid crystals by me it would simply be a case of an optical illusion depending upon the phenomenon that crystals, one end of which touch the glass of a slide, suffer a change of structure so that all the molecular axes become perpendicular to the glass (see *Heidelberg Sitzungsber.*, 1911, No. 22, Table II., Fig. 16 *a—c*) (Note 5). The supposed drops of oleic acid are nothing but a part of the crystal which has become pseudoisotropic and has spread out in little round discs on the glass.

Thus no objections to the explanation of the structures observed as being liquid crystals can be regarded as tenable. They are all in direct opposition to the actual facts. On the other hand, the theory of liquid crystals is not contradicted by a single *fact*, but only by a *hypothesis*, namely, the assumption that the molecules of all so-called modifications and states of aggregation of a substance are identical. It is certainly quite irreconcilable with this assumption (*Zeit. Phys. Chem.*, 1910, lxxi., 355; *Verh. d. Karlsr. Nat. Ver.*, 1913, xxv.). But this only demonstrates the incorrectness of the hypothesis, which may also be deduced from other facts ("Molecular-physik," 1889, ii., 413).

III. *Structure and Form of Liquid Crystals.*

If we bend a sheet of mica, in consequence of the distortion of the molecules or the alteration of their distances, elastic reaction force comes into evidence, and lasts as long as the bending, disappearing when it comes to an end, since inasmuch as the limits of elasticity were not passed the grating arrangement of the molecules remained the same. When a liquid crystal is bent such a lasting elastic reaction force never comes into play; for if by the bending the molecules are momentarily displaced the original grating arrangement is at once spontaneously restored by the action of the molecular directive force, even if the crystal is not bent back. Crystals which flow together thus possess no limits of elasticity, and for this reason must be called "liquid"; for the lack of a limit of elasticity is the special characteristic of the liquid state.

The molecular directive force not only restores the disturbed structure of liquid crystals, but also their altered form. If a piece is broken off a solid crystal the molecular forces cannot fill up the gap, if the crystal is not suspended in a supersaturated solution in which it can again become perfect by the addition of new material. A liquid crystal, on the contrary, at once resumes its normal form, in which equilibrium is restored between the molecular forces among themselves and the thrusts resulting from the thermic state of motion.

I have not yet succeeded in demonstrating this thermic motion in the usual way by observation of the Brownian movement (Rob. Brown, *Pogg. Ann.*, 1828, xiv., 294; J. Perrin, "Les Atomes," Paris, Alkan, 1913; O. Lehmann, *Verh. d. Karls. Nat. Ver.*, 1913, xxv., 41) because it is impossible to obtain little particles continuously in suspension in crystalline liquids. Thus, if an uncovered preparation of para-azoxyphenetol is slightly blackened over a turpentine or magnesium flame, and is then melted under a cover-glass, the Brownian movement among the particles of soot can readily be observed in the isotropic melt. But as soon as the conversion into a crystalline liquid occurs the particles of the growing liquid crystals are driven against the glass walls and remain suspended there, even if the mass is rubbed off in order to try to drive them again into the interior. The experiments of Friedrich, Laue, and others on the bending of the Röntgen rays in crystals (see also M. de Broglie, *Comptes Rendus*, 1913, clvi., 1011, 1153; M. Laue, *Phys. Zeit.*, 1913, [3],

xiv., 423) provide no evidence of thermic movement in them, and it must be assumed that it is negligibly small. Small very rapidly changing etched figures which I observed in the case of para-azoxyphenetol (*Phys. Zeit.*, 1911, xii., 543) might be caused by the state of thermic motion in the corrosive melt. The scintillating polarisation discovered by Ch. Mauguin (*Comptes Rendus*, 1912, cliv., 1359) in semi-isotropic liquid crystalline layers of optically biaxial substances, might be caused by the rapid change of the directions of the secondary axes, while the principal axes or axes of revolution of the molecules which are in the direction of the optical axes remain parallel, as shown by the complete extinction (in a capillary tube) when observed transversely.

Perhaps the thermic movement, *i.e.*, the expansive force, if it exists is anisotropic in the case of liquid crystals, and thus the surfaces turn outwards more forcibly in different places, until the capillary pressure aroused by the dilation again restores equilibrium. The form of a liquid crystal would then be the result of the opposing action of molecular forces and expansive force. On the other hand, that of a solid crystal would be the result of the repelling, attracting, and directing molecular forces. If this is correct the shapes of the liquid crystals must be fundamentally different from those of the solid crystals, which does not appear to be the case. Probably the force which determines the shape of the liquid crystals depends entirely upon the action of the so-called molecular forces, which is certainly difficult to understand from the point of view of the kinetic theory (Note 6).

From the behaviour, already described, of ammonium oleate in capillary tubes, it may be concluded that the molecules are not rod-shaped (in the direction of the principal axis) but leaflet-shaped (perpendicular to the principal axis), since rod-shaped molecules would arrange themselves obliquely to the walls when the mass was poured, owing to the greater velocity in the neighbourhood of the axis of the tube (Note 7). This formation of the molecules is confirmed by the phenomenon that even the power of adsorption of glass or mica plates is capable of producing semi-isotropic structure (*Ann. Phys.*, 1900, ii., 689; 1906, xix., 408; *Phys. Zeit.*, 1910, xi., 575; *Heidelb. Sitzungsber.*, 1912, No. 13, Table II., Fig. 21; F. Wallerant, *Comptes Rendus*, 1906, cxliii., 555; P. Gaubert, *Ibid.*, 1907, cxlv., 722; D. Vorländer, *Zeit. Phys. Chem.*, 1907, lxi., 166; D. Vorländer and H. Hauswaldt, "Acta nova," Halle, 1909, 90). It may be supposed that it compels the molecular discs to arrange themselves parallel to the surface of the plates, *i.e.*, so that the optical axes are perpendicular to the glass. This is confirmed by the fact that this alteration of structure is facilitated by pressing the mass between two plates or by gently pushing one over the other.

The effect of more powerful surface tension, such, for example, as is exerted at the surface exposed to the air, causes the molecular leaflets to arrange themselves parallel to the surface (*Ann. Phys.*, 1903, xii., 332; "Flüssige Kristalle," 1909, Table IX., Figs. 2 and 3).

The assumption that the molecules are disc-shaped is in good agreement with the phenomenon called forced homotropism, viz., when liquid crystalline layers flow rapidly over one another the molecules behave to a certain extent like furniture castors, the axes of which endeavour to become perpendicular to the direction of pushing. The mass thus becomes semi-isotropic in such a way that the optical axis is perpendicular to the direction of thrust, and the inner friction decreases as if the molecules acted as friction wheels, like the resistance of a wheelbarrow provided with guiding wheels, as soon as the wheels have arranged them selves properly (*Ann. Phys.*, 1903, xii., 318; *Zeit. d. Ver. D. Ing.*, 1908, lii., 387).

The spontaneous homotropism of liquid crystals when they flow together (*Zeit. Phys. Chem.*, 1895, xviii., 91) may be explained by supposing that the more or less irregularly arranged discs as they rub against one another exert directive forces on one another in such a way that they all take up the same orientation, at any rate as regards their surfaces. If, as with viscous liquid crystals, the arrangement of the individuals is not too irregular, fan-like structures must be produced, as with the solid crystals of acid ammonium oleate hydrate which has actually often been observed (*cf.*, O. Lehmann, "Flüssige Kristalle," 1904, Table I., Fig. 6; Table II., Fig. 1). This constitutes a transition to the sphaerolithic structure (*Wied. Ann.*, 1895, lvi., 784) which occurs in liquid crystals of ammonium oleate hydrate, if the solution contains much water, partly on account of the increase of surface tension thus produced, and partly on account of the decrease of viscosity (true stiffening) in consequence of the absorption of water (swelling up).

Also when liquid crystals of ammonium oleate are bent fan-like structures appear, inasmuch as on the concave side the molecular axes (directions of extinction) arrange themselves tangentially to the curve of bending, just as when a solid crystal (of, for example, ammonium nitrate, *Zeit. f. Kristallog.*, 1877, i., 110) or orthomercury-ditolyl (*loc. cit.*, 1885, x., Fig. 39) bends. The other molecules then endeavour to become parallel to them, and thus the fan structure is produced.

Allied to these fan structures are the conical and double conical structures (*Wied. Ann.*, 1895, lvi., 786, Figs. 20—26; *Ann. Phys.*, 1903, xii., 329; "Flüssige Kristalle," 1904, p. 40, Table V.; *Ann. Phys.*, 1906, xix., 408, Figs. 1—12; *Verh. d. Phys. Ges.*, 1911, xiii., 338; *Heidelb. Sitzungsber.*, 1911, No. 22, Table IV., Fig. 24; "Die neue Welt der flüssigen Kristalle," 1911, p. 368), which also produce molecular states of equilibrium, which in spite of thermic motion are permanent, and after any distortion of the mass (if it is not too deep-seated) again return to their original form as soon as the strain is removed. In spite of thermic motion they also are permanent, as the arrangement of the molecules corresponds to the molecular directive force, although the molecules are not parallel as in the grating structure or the state of semi-isotropic aggregation. They may be regarded as fan-structures which, being closely connected with one another, are grouped quite symmetrically about an axis, so that if the fan-structure can be explained on the ground of the hypothesis of the leaflet shape of the molecules and their behaviour as astatic systems of magnets (which has not yet been proved mathematically) the explanation of the conical disturbances on the basis of the same hypothesis offers no difficulties. The same holds good for the spiral structures which are produced in uniformly liquid crystalline layers by twisting the limiting anisotropic plates over one another, and also by addition of different non-isomorphic substances (Ch. Mauguin, *Comptes Rendus*, 1910, cli., 886; O. Lehmann, "Die neue Welt der flüssigen Kristalle," 1911, p. 222; *Ann. Phys.*, 1900, ii., 670; "Flüssige Kristalle," 1904, Tables XIV.—XVII.; *Ann. Phys.*, 1905, xviii., 808; *Phys. Zeit.*, 1911, xii., 540; *Ann. Phys.*, 1911, xxxv., 193; 1912, xxxix., 105; *Heidelb. Sitzungsber.*, 1912, No. 13, Table III., Fig. 64).

Speaking generally, we can say, at any rate as far as the hydrate of ammonium oleate is concerned, liquid crystals behave as if they consisted of mobile but approximately rigid leaflet-shaped molecules, which exercise turning moments (couples of forces) upon one another, comparable with those of astatic systems of magnets formed of revolving electrons (in paths which form knots).

Notes.

5. In view of the large amount of water in Herr M.'s preparations it might be thought that hollow liquid sphaerocrystals were observed, the interior of which was filled with isotropic mother-liquor, which can be pressed out if the crust has been converted into solid acid oleate by evaporation of ammonia from the solution. But the substance squeezed out is aqueous solution, not oleic acid.

6. For models to illustrate this, assuming the electromagnetic theory, see "Molecularphysik," 1889, ii., 376;

Phys. Zeit., 1909, x., 553; 1912, xiii., 550; "Die neue Welt der flüssigen Kristalle," 1911, 346.

7. If they were only systems of revolving electrons as shown by the models mentioned above they could be regarded as deformable. In this case the properties of a substance must be altered by deformation, which is not actually the case. But they can behave like rigid discs only if the velocity of motion of the electrons is very great. The phenomena of radio-activity actually reveal such great velocities in the interior of the molecule.

(To be continued).

THE FILTRATION OF BARIUM SULPHATE.

By J. L. OSBORNE.

Krak (*Chemist Analyst*, 1912, p. 26) has recently stated that to filter barium with suction seems a rather daring experiment, even when specially prepared filters are used, but that it may be done as follows:—

"Pour the supernatant liquid through the filter, using suction. Before the precipitate begins to follow, add about 10 cc. of a saturated, slightly acid, solution of ammonium acetate to the precipitate, and stir it up well. The fine $BaSO_4$ changes instantly into a coarse precipitate, and can be washed instantly while suction is going full speed without ever passing through the filter. The results thus obtained are not influenced by the use of the filter solution."

This sounded as though the barium sulphate were coagulated by the ammonium acetate solution. It seemed desirable to verify this and to see what would be the effect of adding solid ammonium acetate to a solution from which barium sulphate had been precipitated cold. A number of experiments were therefore made to determine what happens and what are the limitations of the method, if any.

Equivalent solutions of barium chloride and of sulphuric acid were prepared, and 100 cc. of the barium chloride solution were added a little at a time to 100 cc. sulphuric acid, stirring continuously, and keeping the solutions at 75—80°. The precipitate is coarse enough for ordinary filtration by gravity, but is sucked through a filter-paper when suction is applied. In the next experiment the supernatant liquor was decanted, as recommended by Krak, and 10 cc. saturated ammonium acetate solution were stirred up with the residue. There seems to be a solution of the barium sulphate which re-precipitates as coarser crystals which are not carried through a filter-paper by suction. There is no difficulty at all in duplicating Krak's result.

In another experiment the barium sulphate was precipitated hot as before, but the supernatant liquid was not decanted. About 75 grms. of solid ammonium acetate were added to the solution, making the concentration with respect to this salt practically the same as in the preceding experiment. Filtration by suction was not possible. The whole mixture was boiled for nine to ten hours, but even then the barium sulphate ran through the filter under suction. This showed that a mixture of ammonium acetate and hydrochloric acid behaves quite differently from ammonium acetate alone. This might be due to the free acid or to the chloride preventing the growth of the crystals, or it might be that the chloride had a peptonising action and disintegrated the barium sulphate.

A hot solution of ammonium sulphate was precipitated by adding just sufficient hot barium chloride solution. Since there were about 110 cc. of solution, approximately 100 grms. of solid ammonium acetate was added, and the mixture was boiled for eight hours, four hours at a time with several hours of standing between the two periods. The barium sulphate could then be filtered with suction. This experiment shows that ammonium chloride retards but does not prevent the growth of the barium sulphate crystals.

Some barium sulphate was made filterable by Krak' method. This was boiled for nine hours with an ammonium chloride solution. At the end of this time the crystals filtered as well as before, thus showing that the ammonium chloride solution had no peptonising or disintegrating action.

To determine whether Krak's method worked well with neutral and acid solutions, three sulphate solutions were made up of the same strength, sodium sulphate, sodium sulphate acidified with hydrochloric acid, ammonium sulphate. These solutions were heated to 80°, and sufficient hot barium chloride solution added to ensure complete precipitation. The mixtures were brought to boiling for five minutes, and were then allowed to stand over night. In each case the supernatant liquid was decanted, 5 cc. of saturated ammonium acetate added, and the solution boiled for five minutes. The precipitates did not filter well, so 10 cc. more of ammonium acetate solution were added to each beaker. Each solution was boiled for one minute, and then allowed to stand. There was no difficulty in filtering with suction, the three lots behaving practically alike.

The last experiments dealt with cold precipitation of sulphuric acid by barium chloride. After decantation, ammonium acetate solution was added, and boiling was kept up for eight to ten hours. It was quite impossible to filter the barium sulphate. The experiment was repeated with 20 cc. ammonium acetate solution, boiling steadily for ninety-six hours, using a reflux cooler. At the end of this time the barium sulphate filtered nicely with full suction.

These experiments clear up the theory of the process. Barium sulphate is soluble in ammonium acetate solution, and the crystals therefore grow in a hot solution. If the barium sulphate is precipitated under conditions such that the crystals are nearly large enough to permit of filtration with suction, a short heating is enough to make them grow to the required size. If the barium sulphate is precipitated cold, the crystals are small, and a very much longer heating is necessary to give the required size. Since ammonium chloride and hydrochloric acid do not peptonise or disintegrate the barium sulphate crystals and yet do retard the growth, it is clear that these substances decrease the solubility of barium sulphate in ammonium acetate solutions.

This work was suggested by Prof. Bancroft, and has been carried on under his supervision.—*Journal of Physical Chemistry*, xvii., No. 7.

A STUDY OF THE METALLIC TELLURITES.*

By VICTOR LENHER and EDWARD WOLESENSKY.

Since the early work of Berzelius very little has been contributed to the chemistry of the tellurites (*Jahresb.*, 1833; *Pogg. Ann.*, 1833, xxviii., 396; *Kongliga Svenska Vetenskaps Akademiens Handlingar*, 1833, 277; *Pogg. Ann.*, 1834, xxxii., 1—577; *Ann. Chim. Phys.* [2], 1835, lviii., 225). What work has been done has been largely incidental rather than a systematic study.

In our work the tellurites of potassium, sodium, silver, barium, magnesium, cadmium, nickel, cobalt, manganese, lead, and ammonium were studied. In addition to the normal tellurites, the di- and tetratellurites of the alkali metals were also studied. The normal and ditellurites of potassium and sodium were prepared by fusing tellurium dioxide with the calculated quantities of the alkali carbonates. The tetratellurites of potassium and sodium were obtained by the decomposition of the corresponding ditellurites with water. The tellurites of the other metals were prepared by precipitation from solutions of their salts (usually the chlorides) by means of sodium tellurite.

* *Journal of the American Chemical Society*, xxxv., No. 6.

The tellurium dioxide used was prepared from elementary tellurium by solution in aqua regia and precipitation from the hydrochloric solution by sodium bisulphite. The impure tellurium thus obtained was fused with an excess of potassium cyanide, the fusion extracted with hot water, when a solution was obtained of potassium telluride, selenocyanate, and thiocyanate. The insoluble residue was invariably refused and treated again as before.

Air was then bubbled through the solution, precipitating the tellurium, while the seleno- and thiocyanates were unaffected. The tellurium, after filtering and washing, was dissolved in dilute nitric acid and re-crystallised as the basic nitrate. The nitrate was finally heated strongly in a platinum crucible, and tellurium dioxide obtained. The dioxide was then fused, to insure complete removal of oxides of nitrogen. The product was perfectly white.

Methods of Analysis.

In the analysis of the tellurites studied, the following methods were used. Water was usually determined by loss of weight on heating. In some cases a temperature of 450° was necessary for the complete dehydration of the substance, but in such cases it was not necessary to continue the heating for more than 15 minutes. In the case of the alkaline tellurites, on account of the oxidation of these salts on heating in the air, it was also deemed advisable to weigh the water directly, after first absorbing in sulphuric acid.

The tellurium and basic element were then separated by one of the following general methods:—(1) Volatilisation of the tellurium oxide in a stream of hydrochloric acid gas. This method was used by Hutchins in the analysis of a number of tellurates (*Journ. Am. Chem. Soc.*, 1905, xxvii., 1157). (2) Precipitation of the tellurium in presence of the other metal, by means of sulphur dioxide and hydrazine hydrochloride, and the subsequent determination of the base in the filtrate by one of the usual methods (Lenher and Homberger, *Ibid.*, 1908, xxx., 387).

The first of these methods is not applicable to the tellurites of those metals whose chlorides are sensibly volatile. It was used in the analysis of the potassium, sodium, silver, and lead salts. A weighed amount of the substance to be analysed was placed in a porcelain boat and heated in a combustion tube in a current of hydrochloric acid gas. That part of the tube which contained the boat was surrounded by a sheet-iron jacket, leaving an air space of about one inch between the jacket and the glass tube. The object of this arrangement was to make the heating more uniform. The tellurium was volatilised as $TeO_2.2HCl$. The greater portion of the tellurium was condensed in the cooler part of the tube. The excess of hydrochloric acid together with a little tellurium was absorbed in water.

The chloride remaining in the boat was weighed and calculated as metal. The tellurium sublimate in the glass tube was washed into a beaker, and the solution from the wash-bottle was added. After concentrating this solution, the tellurium was precipitated by means of sulphur dioxide and hydrazine hydrochloride.

Potassium Tellurite.—The normal salt was prepared by fusing in a platinum crucible a mixture of equimolecular quantities of potassium carbonate and tellurium dioxide. The mixture fused quite readily, giving off carbon dioxide. In order to prevent oxidation to tellurate, the air in the crucible was displaced by a stream of carbon dioxide from a generator. On cooling, a white crystalline mass was obtained, which was deliquescent and extremely soluble in water. The aqueous solution slowly deposited tellurous acid on exposure to air, and more readily when air was bubbled through the solution. On heating, however, the precipitate again dissolved, showing that at higher temperatures tellurous acid will displace carbonic acid.

A small amount of a strong solution of this substance was allowed to evaporate in a desiccator over sulphuric acid. Another vessel containing solid potassium hydroxide was placed within the desiccator to absorb the carbon dioxide of the air. The solution did not crystallise, but on evaporation it gradually formed a thick syrup, which finally solidified. The product was a hard, transparent and homogeneous mass, having a waxy or resinous appearance without the slightest external indication of crystallisation.

Two successive portions of this material were obtained, as it solidified from solution, and were analysed, with the following results:—

Calculated for $K_2TeO_3.3H_2O$.—K, 25·43; Te, 41·44; H_2O, 17·54.
Found I.—K, 25·25; Te, 40·62; H_2O, 17·71.
Found II.—K, 25·82; Te, 40·83; H_2O, 17·09.

These results indicate that although potassium tellurite, when prepared as described, cannot be crystallised from an aqueous solution, it is nevertheless a definite compound, $K_2TeO_3.3H_2O$. This compound was also prepared by treating tellurium dioxide with a solution of caustic potash, either cold or hot. The combination seems to take place only in the proportion of $2KOH : TeO_2$, so that if we have more than this proportion of tellurium dioxide, some will remain undissolved. Tellurium dioxide dissolves in a hot solution of potassium carbonate, although not so readily as in caustic potash.

Potassium Ditellurite.—Potassium ditellurite was prepared by fusing together 1 grm.-molecule of potassium carbonate and 2 grm.-molecules of tellurium dioxide. It fuses more readily than the normal salt, and on cooling appears as a white crystalline mass.

Potassium ditellurite is insoluble in cold water. It dissolves in boiling water, but on cooling the solution decomposes, yielding the normal tellurite, which remains in solution, and the tetratellurite which is precipitated. The ditellurite decomposes slightly even at the boiling temperature, for complete solution of the substance was never obtained.

Potassium Tetratellurite.—Berzelius obtained the tetratellurite of potassium by boiling a solution of potassium carbonate with tellurium dioxide, filtering the boiling solution, and allowing to cool slowly. The tetratellurite separated out in the form of small grains attached to the walls of the vessel. During the present work the tetratellurite was prepared by the decomposition of the ditellurite with water. Finely pulverised ditellurite was boiled with water for a short time. The hot solution was quickly filtered. White shining flakes separated out as the solution cooled. The compound was analysed, and its composition found to conform to the formula $K_2Te_4O_9.4H_2O$.

Calculated—K, 9·73; Te, 63·41; H_2O, 8·95.
Found I.—K, 9·76; Te, 64·51; H_2O, 8·61.
Found II.—K, 10·00; Te, 64·20; H_2O, 8·35.

This salt when boiled with its mother-liquor dissolves, but separates again on cooling. Prolonged treatment with boiling water decomposes it, leaving tellurium dioxide as the final product. A quantity of the salt which had been washed repeatedly on the filter with boiling water left a white powder which contained 0·66 per cent water, 0·47 per cent potassium, and 78·52 per cent tellurium. It was therefore nearly 99·0 per cent tellurium dioxide. It is probable that the carbon dioxide of the air played a part in this decomposition.

Sodium Tellurites.—Normal sodium tellurite was prepared in a manner similar to that by which the corresponding potassium salt was obtained. The properties of these two salts are quite similar. Sodium tellurite is readily soluble in water. It is not deliquescent, and can be crystallised from solution in the form of broad, flat plates of hexagonal outline. It was also obtained in slender needles, grouped in radiating clusters. The evaporation of the solution was conducted in the same manner as with the potassium salt, namely, in a desiccator over sulphuric acid and solid caustic potash.

Unlike potassium tellurite, which contains three molecules of water, sodium tellurite contains five molecules of water of crystallisation, $Na_2TeO_3.5H_2O$.

Calculated—Na, 14·79; Te, 40·94; H_2O, 28·88.
Found I.—Na, 14·72; Te, 40·33; H_2O, 28·89.
Found II.—Na, 14·77; Te, 40·49; H_2O, 29·14.

An interesting, though not unusual, case of equilibrium was discovered in the system, sodium tellurite, water, and alcohol. If to a strong solution of sodium tellurite we add about twice its volume of 95 per cent alcohol, the two liquids do not mix. There is, however, a redistribution of the water between the alcohol and the tellurite. The alcoholic layer increases in volume by abstracting water from the tellurite solution, while the latter becomes more concentrated. Long standing and repeated shaking will not produce any further changes in this system. If, now, we add solid sodium tellurite, it will slowly dissolve, increasing the volume of the tellurite solution and withdrawing water from the alcoholic layer. But if we add, instead, about five volumes of absolute alcohol, the water is almost completely withdrawn from the sodium tellurite and the latter is precipitated. Potassium tellurite and alcohol behave similarly.

The sodium di- and tetratellurites are analogous to the corresponding potassium salts, both in their methods of preparation and in their properties. Both of these compounds fuse below a red heat, and on cooling form clear glasses. The ditellurite, like the corresponding potassium salt, can also be obtained crystalline by fusion. The tetratellurite, when prepared by decomposing sodium ditellurite with water, has the composition $Na_2Te_4O_9.4H_2O$.

Calculated—Na, 5·97; Te, 66·07; H_2O, 9·32.
Found I.—Na, 6·06; Te, 65·78; H_2O, 9·64.
Found II.—Na, 5·78; Te, 66·35; H_2O, 9·43.

Ammonium Tellurite.—Berzelius attempted to prepare ammonium tellurite by dissolving tellurous acid in ammonia and then adding ammonium chloride or alcohol. In both instances he obtained a flocculent precipitate, which was insoluble in water but dissolved readily in ammonia. He also obtained the same substance by warming a solution of ammonium carbonate with tellurous acid or tellurium tetrachloride, and adding ammonium chloride. On heating this compound, ammonia was evolved, and a residue of tellurium dioxide remained. The amount of this residue in one case was 83·1 per cent; in another it was 83·87 per cent, while the calculated amount of tellurium dioxide in the compound $(NH_4)_2Te_4O_9.4H_2O$ is 83·7 per cent. He therefore concluded that his precipitates were tetratellurites, exactly analogous in composition to the corresponding salts of potassium and sodium. Berzelius also evaporated to dryness, with the aid of gentle warming, a solution of tellurous acid in ammonia. He found the residue to be principally hydrated tellurium dioxide containing a little ammonia.

In the present work tellurium dioxide was dissolved in ammonium hydroxide (sp. gr. 0·91) by heating in sealed tubes for 10 hours at a temperature of 95—100°. After cooling and filtering the solution was allowed to evaporate spontaneously. As the solution evaporated, small crystals were obtained in the form of short needles arranged in radiating groups, or clusters of thin transparent plates. On drying these became opaque. They dissolved readily in ammonia, but were insoluble in water.

They were analysed as follows:—A weighed amount of the residue was placed in a porcelain boat inside of a glass combustion tube. This tube was connected to an absorption apparatus containing a standard solution of sulphuric acid. While a slow current of dry air was drawn through the tube, the boat was heated, gently at first, increasing the temperature gradually to the full heat of the Bunsen burner. A considerable amount of moisture was condensed upon the cooler part of the tube. The residue in the boat was weighed as tellurium dioxide. The excess of acid in the absorption apparatus was then titrated with standard alkali, and the amount of ammonia estimated. The water was estimated by difference.

The following composition was found:—Ammonia 1·69 per cent, tellurium dioxide 89·19 per cent, and water 9·12 per cent. This would correspond to the formula $NH_3.5TeO_2.5H_2O$ or $5H_2TeO_3.NH_3$. It is not believed that this is a definite compound. It is more likely that this is but one stage in the decomposition of ammonium tellurite to hydrated tellurium dioxide. The crystals obtained from the ammoniacal solution were probably a definite ammonium tellurite. This compound, however, is so unstable that it can exist only in solution, or when surrounded by the mother-liquor, and when dried it spontaneously decomposes, even at the ordinary temperature.

(To be continued).

A METHOD FOR THE QUALITATIVE ANALYSIS OF THE ZINC GROUP.*

By RICHARD EDWIN LEE, ROY H. UHLINGER, and FRANK O. AMON.

(Concluded from p. 183).

(c) *Procedure and Notes. Procedure* II.—The group precipitate (P. 1) which consists of ZnS, MnS, CoS, and NiS is transferred to a casserole and treated with 10—20 cc. of HCl (1 : 12). Stir the mixture thoroughly for 2—3 minutes; if a black residue remains the presence of Ni and Co are indicated and a few crystals of $KClO_3$ should be added. Boil the mixture for a few minutes, dilute with a little water, and filter off the yellow residue of sulphur. Evaporate the filtrate to a few cc. to remove excess of acid; add 10—20 cc. of water and make slightly alkaline with 5N NaOH. If the precipitate which forms is so large that the mixture becomes gelatinous, add 10—20 cc. of water, cool the mixture and add solid Na_2O_2 in very *small* portions until a steady evolution of gas continues after the mixture has been well stirred. Heat to incipient boiling and filter (Precipitate, P. 4; Filtrate, P. 3).

Notes.

(1) The MnS and ZnS usually dissolve readily in cold HCl (1·12); the NiS and CoS are quite soluble in concentrated HCl but dissolve very slowly (see T. E., Series III.). If a black residue remains after the treatment with HCl the presence of Co and Ni is indicated. The absence of a black residue does not prove, however, that Ni and Co are not present in the precipitate.

All the sulphides of this group are readily soluble in HCl (1·12) and $KClO_3$. The group precipitate is first treated with HCl in order to obtain indications as to the presence of Ni and Co. HCl and $KClO_3$ are used to dissolve the precipitate in preference to *aqua regia*, since much free sulphur is formed at the start if the latter is used.

(2) NaOH completely precipitates Mn and Ni as $Mn(OH)_2$ and $Ni(OH_2)$; these substances do not dissolve in a moderate excess of this reagent. The $Zn(OH)_2$ dissolves readily, however, in an excess because it is an amphoteric substance. The product of the reaction is sodium zincate, $Na_2Zn_2O_2$ (see T. E., Series VI.). If an excess of NaOH be added to $Co(OH)_2$ a portion, of the latter dissolves forming a blue solution, the colour of which is due, probably, to Na_2CoO_2. Therefore, great care must be exercised to avoid an excess until the cobalt is oxidised to the "-ic" condition.

The Na_2O_2 converts the $Zn(OH)_2$ into soluble Na_2ZnO_2, $Mn(OH)_2$ into a brown $MnO(OH)_2$, $Ni(OH)_2$ into black $Ni(OH)_3$, and $Co(OH)_2$ into black $Co(OH)_3$.

(3) The Na_2O_2 is added to a cold solution, as it decomposes with explosive violence when the solution is hot. Oxygen is liberated during the decomposition. Boiling decomposes excess of sodium peroxide.

(4) The separation of zinc by this method is very satisfactory. When the directions have been followed care-

* *Journal of the American Chemical Society*, xxxv., No. 5.

fully the filtrate is free from Ni and Co, which usually interfere with the later tests for Zn.

Procedure III.—The filtrate obtained from P. 2 contains sodium zincate. Acidify the solution with acetic acid, $HC_2H_3O_2$, warm to about 70°, and saturate with H_2S. A white, flocculent precipitate, ZnS, confirms the presence of Zn. If results are doubtful, the confirmatory tests may be continued as follows;—Filter, wash the precipitate of ZnS, then dissolve it in the least amount of HNO_3. Evaporate nearly to dryness to expel excess of acid, neutralise with a few cc. of Na_2CO_3 solution. Add a volume of $Co(NO_3)_2$ equal to that of one-sixth the solution in the casserole, evaporate to dryness and ignite gently. A green residue, ZnO.CoO, or $CoZnO_2$, confirms Zn.

Notes.

(1) Zn is precipitated readily from warm dilute $HC_2H_3O_2$. If but fractions of a mgrm. are present the precipitate coagulates slowly; therefore care must be exercised or the precipitate will be missed.

(2) If a white flocculent precipitate forms at once when the $HC_2H_3O_2$ solution is treated with H_2S, a confirmatory test is unnecessary as the action is highly characteristic of Zn. Mn is the only other element of the group which forms a light coloured sulphide and it is not precipitated in the presence of acetic acid.

(3) The composition of the green salt obtained in the confirmatory test for Zn is probably represented by the formula $CoZnO_2$. A large excess of Co salt should be avoided, as the black colour of CoO obscures the green colour.

Procedure IV.—The Na_2O_2 precipitate (P. 2) which contains $MnO(OH)_2$, $Ni(OH)_2$, and $Co(OH)_3$ should be washed thoroughly to insure the removal of the soluble adhering zinc salt, then transferred to a casserole and dissolved in the least quantity of warm HCl (1 : 12). Filter to remove paper and evaporate filtrate to about 2 cc. Add 5 cc. of HNO_3 (1 : 20), boil until the reddish brown fumes cease to be given off, then add 10—20 cc. of HNO_3 (1·20), heat to boiling and add several crystals of $KClO_3$, continue to boil gently for several minutes. Cool the mixture and allow any suspended matter (probably a precipitate of MnO_2, if it has a brown colour) to settle. Decant the liquid through an asbestos filter in such a manner that most of the precipitate (if there is one) remains in the casserole. Test the filtrate by boiling it with a crystal of $KClO_3$. Filter if more precipitate forms (Precipitate, P. 5; Filtrate, P. 6).

Notes.

(1) Manganous salts of the type of $MnCl_2$ are rapidly oxidised to MnO_2 by $KClO_3$ in the presence of HNO_3 (see T. E., Series VIII.). As MnO_2 is readily soluble in the presence of reducing agents all fragments of filter paper must be removed from the HNO_3 solution. The HCl must be removed previously by evaporation, since it reacts with HNO_3 to form oxides of nitrogen in which MnO_2 is readily soluble. The separation of manganese by this method is very satisfactory; small fractions of a milligrm. of the metal are easily detected.

(2) The MnO_2 is filtered off by means of an asbestos filter. This filter is easily prepared by placing a small loose plug of glass-wool well down in the apex of the ordinary glass funnel, and spreading a large layer of asbestos over it. If filtration is slow, suction may be used.

Students in this laboratory have experienced no trouble whatever in executing the various steps described in this procedure.

Procedure V.—Place the $KClO_3$ precipitate (P. 4) in a casserole, add 20 cc. of HNO_3 (1 : 40), boil for a few minutes, add 1 grm. of PbO_2, and boil again for 2—3 minutes. Pour the mixture into a test-tube, and allow any suspended matter to settle. A pink or violet coloured solution confirms manganese.

Notes.

(1) When Mn is precipitated as MnO_2 by $KClO_3$ in HNO_3 solution, the confirmatory tests are really superfluous, as this reaction is highly characteristic of Mn.

Procedure VI.—Evaporate the filtrate from the $HClO_3$ treatment (P. 4) to about 5 cc. to expel excess of acid, add 10—15 cc. of water, filter, if turbid, then add NaOH solution, drop by drop, until the solution is neutral, or until a permanent precipitate begins to form. Divide the mixture into two equal parts. Test one for Co by Procedure VII., and the other for Ni by Procedure VIII.

Procedure VII.—Add $HC_2H_3O_2$ to one-half the neutral solution obtained in P. 6 until it is barely acid in reaction, then add an equal volume of a saturated solution of KNO_3. Warm the mixture, and allow to stand for an hour if a precipitate does not form sooner. A yellow pulverulent precipitate, $K_3Co(NO_2)_3$, indicates Co. Filter, wash the precipitate with KNO_2 solution, and test it with a borax bead. A blue colour confirms Co.

Notes.

(1) The yellow pulverulent precipitate, potassium cobaltic nitrite, $K_3Co(NO_2)_6$, forms slowly. Therefore it is advisable to allow the precipitate to stand for an hour. However, distinct tests are obtained in twenty minutes when 0·0003 grm. of Co are present, although precipitation is not complete after four hours. The yellow precipitate is slightly soluble in water, but not in a strong solution of KNO_2, owing to the presence of the common ion, $K+$.

(2) The theory of the formation of the salt is indicated by the following equations:—

$$+NO_2^- + H + C_2H_3O_2^- \rightleftharpoons H + NO_2^- + K + C_2H_3O_2^+,$$

$$Co^{++} + (C_2H_3O_2^-)_2 + 2K + NO_2^- \rightleftharpoons Co^{++} + (NO_2^-)_2 + 2K + C_2H_3O_2^-,$$

$$Co^{++} + (NO_2^-)_2 + 2H + NO_2^- \rightleftharpoons Co^{+++} + (NO_2^-)_3 + H_2O + NO,$$

$$Co^{+++} + (NO_2^-)_3 + 3K + NO_2^- \longrightarrow K_3Co(NO_2)_6.$$

(3) Nickelous salts are not oxidised by nitrous acid, HNO_2, and are not precipitated by KNO_2, except in very concentrated solutions. By diluting the solutions as directed the precipitation of Ni is avoided. Potassium nickelous nitrite, $K_4Ni(NO_2)_6$, is dark yellow to red in colour. (See Lang, *Journ. Prakt. Chem.*, 1862, lxxxvi., 299; Hampe, *Ann.*, 1863, cxxv., 346; and Richards, *Chem. Ztg.*, 1904, xxviii., pp. 479, 885, 912).

Procedure VIII.—Add KCN to the other portion of the neutral solution (P. 6) until the precipitated cyanides just re-dissolve. Heat the solution (do not boil) with frequent stirring for two or three minutes. Filter off any residue that may be present. Add a relatively large amount of NaOH solution, then bromine water until the reddish brown colour of the bromine water persists. A black precipitate, $Ni(OH)_3$, indicates Ni. The borax bead test may be used to confirm Ni.

Notes.

(1) The addition of KCN to the neutral solution containing Ni and Co salts results in the precipitation of green $Ni(CN)_2$ and brown $Co(CN)_2$. These cyanides dissolve readily in excess of KCN, forming the soluble complex cyanides $K_2Ni(CN)_4$ and $K_4Co(CN)_6$. The cobalt salt readily undergoes oxidation when in the presence of air, and tends to pass from the cobalto-cyanide to the cobalti-cyanide, thus:—

$$2K_4 + [Co(CN)_6]^{\equiv\equiv} + O + H_2O \rightleftharpoons 2K_3 + [Co(CN)_6]^{\equiv} + 2K + OH^-.$$

The complex nickel salt is more stable in the air, and moreover forms no compound corresponding to the cobalticyanide. However, in the presence of strong oxidising agents like chlorine, bromine, or the hypochlorites in alkaline solution, the complex nickelous salt is oxidised to

the nickelic state, in the form of a simple salt, which is then precipitated as black $Ni(OH)_3$. The final results of the reaction may be formulated as follows:—

$$2K_2Ni(CN)_4 + NaClO + 5H_2O \rightarrow 2Ni(OH)_3 + NaCl + 4KCN + 4HCN.$$

Hence, under the same oxidising treatment the potassium cobalto-cyanide is converted into the soluble potassium cobalti-cyanide, while the potassium nickelous-cyanide is converted into the insoluble $Ni(OH)_3$, and may be separated by filtration.

The cobalt is not precipitated, probably because the complex ion $[Co(CN)_6]^{\equiv}$ is so slightly dissociated into Co^{+++} and CN^{-} ions.

Summary.

(1) Attention has been directed again to the well-known fact that the methods which are generally used in qualitative chemical analysis have received but little systematic study and are in need of revision.

(2) A comparison of a large number of methods for the precipitation and analysis of the Zinc Group as outlined by the respective authors has been made, and the inaccuracies and discrepancies of the procedures noted.

(3) A method has been formulated by which the difficulties usually encountered in attempting the complete precipitation of zinc, manganese, nickel, and cobalt have been overcome without introducing intricate procedures. By a series of test experiments it has been shown that a quantity as small as 0·0005 grm. of any one of the metals in the presence of large amounts of any or all of the other metals may be readily detected.

(4) In the second part of the paper, which relates to the subsequent analysis of the group precipitate, it has been shown that the usual methods of procedure are entirely inadequate for making an accurate analysis, and that the methods proposed in this paper are adequate for confirming even 0·0005 grm. of any of the metals of the group.

(5) The accuracy and general utility of the proposed methods have been proven, as shown by Series XII. of the Test Experiments.

THE SCIENTIFIC WEEK.

(From Our Own Paris Correspondent).

MEDIÆVAL SCIENCE.

M. Pierre Duhem, who has just finished a third volume consecrated to Leonardi da Vinci, has attempted to rehabilitate the scholars of the Middle Ages. It is believed in a general way that the discoveries of the celebrated painter, who was at the same time a great engineer and a great philosopher, owed nothing to mediæval science. In a letter addressed to the Academy, M. Duhem complains that "the scholars of the Renaissance are always placed in opposition to Aristotle, as if human thought had absolutely come to a standstill during the Middle Ages." Now such is not the case. According to the researches of M. Duhem, it seems that the scholars of Paris had already, in the fourteenth century, founded a dynamic which is not opposed to the one of which Leonardi da Vinci established the principles in the beginning of the sixteenth century. Albert de Saxe, Buridan, Nicolas, Oresne were precursors of Leonardi da Vinci.

TWO COMETS VISIBLE IN THE SKY.

The hazy sky of the last few days has prevented the astronomers of the Paris Observatory from observing a new comet, the *Westphal* Comet that was lately discovered in Piata on September 26 last. Its brilliancy, which is at present weak, will very probably increase next month. At present this comet of the seventh or eighth magnitude is not visible to the naked eye. But a simple spy-glass is sufficient to enable one to see this star, the nucleus of which is nebulous and the coma round, and is now shining in the constellation of Versean. From recent observations this comet has been identified with a comet that had not been seen since 1852. It is, then, a new periodical comet that has just been discovered in the heavens, the period of which appears to be of sixty-one years. The number of periodical comets not being very high—not more than a score—this astronomical discovery is important. Since the beginning of the present year four new comets have been signalled by the observatories of the different countries. The comet 1913 *b*, whose spectrum has just been studied by M. Bosler at the Meudon Observatory, is the Metcalf Comet. In a note presented before the Academy of Sciences by M. Deslandres, M. Bosler indicates the presence of hydrocarbons and cyanogen in the atmosphere which is the normal composition of comets.

THE COMMITTEE OF ENQUIRY ON THE METRE.

The members of the International Committee of the Metre, which met on October 10 at the Ministry of Commerce to register recent progress of the metrical system, and to study the improvements yet to be brought to bear upon it, were present at the sitting of the Academy of Sciences. M. Derboux, perpetual secretary, welcomed MM. Foerster, chairman, Blaserna, secretary, Egorof, delegate from Russia, Gautier, director of the Observatory of Geneva, von Lang, member of the Academy of Science of Vienna, Tanakadate, of the University of Tokio, who were seated in the space reserved for the members of the Paris Institute. In presenting the reprint of the official reports of the Academy of Sciences from 1808 to 1811, M. Darboux recalled to mind the fact that one of the first decennial prizes founded by Napoleon I. was awarded to the authors of the studies that served as the basis of the metrical system.

COCHINEAL DEVOURS CERTAIN NOXIOUS INSECTS.

Some years ago the orange trees and lemon trees of California were ravaged by an insect, to which entomologists have given the barbarous name of *Iceria purchasi*. A learned American discovered an Australian cochineal, *Novius cardinalis*, which had been created by Nature on purpose to devour these devastating insects. Mr. Riley brought some of these cochineals from Australia, and in less than a month they reduced the *Iceria* to infinitesimal and insignificant numbers. These insects appeared in Portugal and in Italy in 1910. The French coast had remained unmolested. But in the month of May, 1912, the owner of a garden situated in the peninsula of Cape Ferrot in the department of the Alpes Maritimes sent to the Minister of Agriculture an unknown insect which was immediately recognised as the terrible *purchasi*. M. Marchal, Member of the Academy of Sciences, who relates this interesting story, had eight cochineals sent from Portugal and from the Portici Laboratory in Italy. One month after numerous descendants of these *Novius* were sent to the gardens of Cape Ferrot. Squads of a hundred cochineals were deposited on the attacked orange trees and lemon trees. In June and July last one could almost think that the noxious insects had been completely eradicated; but M. Marchal has noticed, however, that whole colonies of these insects yet remain. But the cochineals chase them unceasingly, and in the end the victory must be theirs.

WIRELESS TELEGRAPHY SIGNALS.

A new crystal detector, into which two physicists, MM. Dongier and Brazier, have passed an alternating current, has enabled these *savants* to make Hertzian waves, sent by the Eiffel Tower, to be heard in specially satisfactory conditions. At the Paris Observatory, by the help of an antenna only 30 metres high, MM. Dongier and Brazier, by uniting the detector to a phonographic pavilion, have been able to hear the crackling of the long or short sparks of the wireless telegraphy at 20 metres from the acoustic trumpet. It is Prof. Bouty who communicated the notice

of the two physicists to the Academy of Sciences. If the ear is placed at the entrance of the acoustic trumpet, the antenna may be reduced to 3 metres in height.

A New "Curie."

The last International Congress of Radio-activity which was held in London in March, 1912, defined the unity of radio-activity to which has been given the name "Curie," in remembrance of the marvellous discovery of radium by M. and Mdme. Curie. This unity corresponds to the state of equilibrum of a grm. of pure radium with two-thirds of a cubic milimetre of emanation. This state of equilibrium indicates that in these particular conditions radium does not give off any more enanation. But the Curie could hardly be employed practically, this unit of measurement being much too large. A physicist, M. Marckwald, has just proposed a new definition of the Curie. He has noticed, after numerous experiments, that in the most varied pitchblendes the relation of pure radium to uranium was a constant, equal on an average to three 10-millionths. To this constant the Professor wishes to give the name of Curie. In the pitchblendes the amount of uranium varies from one to eight, the richest in uranium being the pitchblendes of Western Africa; but, however, the relation of radium to uranium remains invariable. It is highly probable that the new Curie, the application of which may be important in the study of the physics of the globe, of the radio-activity of thermal waters, &c., will be adopted by the next International Congress.

A New Mountain Observatory.

France has lately become possessed of a new Mountain Observatory. Two engineers of Geneva, MM. Honegger and Amiet, have, indeed, just established an observatory destined for the study of physical astronomy of spectrography and meteorology at Saleve, in the Haute-Savoie. This mountain, whose altitude is 1365 metres, generally rises above the mists and fogs that hide the sky of Geneva during the winter nights. Thus numerous observations may be made in satisfactory atmospheric conditions, with the help of a large telescope with an aperture of one metre in diameter, that has been installed on Mount Saleve by M. Schaer, an astronomer of the Observatory of Geneva. The high mountain meteorological observatories are four in number. They are the observatories of the Puy de Dôme, at an altitude of 1460 metres; of the Pic du Midi at 2850 metres; of the Mount Ventoux in the department of Vaucluse at 1900 metres; and lastly that of the Aigonal, formed by a forestry station of the Cevennes at 1550 metres, near the little village of Vallerauque. Two meteorological stations of less importance are to be found; one on Mount Monnier at 2740 metres above Nice; the other on the Ballon de Servance, in the Vosges mountains, at a height of 1200 metres. From each of these six stations, now increased to seven by the creation of the observatory of Saleve, meteorological despatches are sent every day to the central bureau of Paris. As to the astronomical observatories, France possesses eight, without counting those of Algiers and the Salève. These observatories are situated at Paris, Meudon, Bescançon, Saint-Genis-Laval near Lyons, Marseilles, Nice, Toulouse, and Floirac, near Bordeaux.

A New Parachute.

A new aviator's parachute has just been invented by an officer attached to the aeronautic service at Vincennes, Captain Couade of the Engineers. The delicate point of these parachutes consists, as is well known, in the manner of assuring the development of the parachute, at the right moment, without any possible mishap. M. Lecorum, who has presented Captain Couade's notice to the Academy of Sciences, showed that the problem had been solved very ingeniously by means of a little auxiliary parachute, which, placed at the back of the aeroplane, is joined to the large parachute by a direct machinery. A simple manœuvre can unfasten the little parachute, which, under the influence of the speed of the aeroplane, draws back the large parachute and causes its development. The resistance of the large parachute is so great that the aeroplane upheld descends gently and vertically to earth. To avoid any sudden movements a brake regulates the manœuvre of the development of the little auxiliary parachute.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Academie des Sciences. Vol. clvii., No. 4, July 28, 1913.

Sulphur Liberated by the Action of Water on Sulphurous Acid.—E. Jungfleisch and L. Brunel.—The sulphur set free by the decomposition of sulphurous acid is soft sulphur, but its state is dependent upon the temperature at which the separation occurs. Above 113°, the melting-point of octahedral sulphur, it is fused to a liquid which on cooling crystallises in a form which differs according to the temperature. If the mixture is kept below 100° the sulphur still fuses, and after fusion is precipitated in crystalline masses or in liquid droplets which finally crystallise. At 68—70° it separates in the form of very minute spherical globules, which form agglomerations when heated. In this state the substance has the characteristic properties of soft sulphur. When the reaction between sulphurous acid and water takes place at the ordinary temperature it occurs very slowly, and the sulphur formed is crystalline.

Negative Photocatalysis of Hydrogen Peroxide.—Victor Henri and René Wurmser.—When traces of various substances, *e.g.*, soda, iodine, are added to hydrogen peroxide it becomes stable towards the ultra-violet rays. It is possible that in many cases of catalysis by ferments or colloidal metals the poisons or antiferments act upon the substance undergoing transformation, and not upon the diastase or catalyst. There is a very close relation between the action of certain ferments and that of the ultra-violet rays.

Quantitative Separation of Chromium and Aluminium. Analysis of Chromite.—F. Bourion and A. Deshayes.—The separation of chromium and aluminium can be effected by subjecting them to the action of a mixture of chlorine and sulphur dichloride, which gives satisfactory results, provided that ammonium sulphate is added to the mixed oxides if more than 20 per cent of chromic oxide is present. With mixtures containing less than 50 per cent of chromic oxide there is always a small residue which is not attacked. In order to bring about the complete chlorination of chromite the mineral must previously be heated to a red heat with mercuric sulphate. After chlorination the constituents of the mixture can be separated into three groups:—(i.) The non-volatile chlorides of magnesium and calcium; (ii.) the volatile chloride of chromium which is insoluble in water; (iii.) the volatile chlorides of iron and aluminium which are very soluble in water. This method of analysing chromite is very rapid, but the silica (which remains with the non-volatile chlorides) cannot be estimated by means of it.

No. 5, August 4, 1913.

Absorption of Ultra-violet Rays by Mineral Dyes in Aqueous Solution.—MM. Massol and Faucon.—Different mineral colouring matters, *e.g.*, potassium ferrocyanide, copper sulphate, potassium chromate, absorb the invisible ultra-violet rays unequally. The absorbent action of synthetic organic dyes is much greater than that of the mineral dyes, but it is of the same order qualitatively, and broad absorption bands, if they exist, are found in the same regions of the spectrum.

Rôle of Uranium Salts as Photochemical Catalysts.—Daniel Berthelot and Henry Gaudechon.—No fluorescent or radio-active substances which the authors have examined accelerate photochemical reactions, with the exception of uranium salts. The action of the uranium salts is limited to a special class of reactions, namely, the decomposition of linear acids, particularly if they are dibasic or complex. These reactions occur spontaneously in ultra-violet light, but the photocatalyst makes them take place in visible light; thus it lowers the vibratory frequency of the photochemical reaction in the same way as an ordinary catalyst lowers the temperature of a chemical reaction.

Products of Incomplete Reduction of Ceric Oxide.—A. Damiens.—In 1902 Sterba described a new compound which he called cerium oxycarbide, $CeC_2.2CeO_2$. He obtained it by the action of a limited quantity of carbon upon ceric oxide, in Moissan's electric furnace. The investigation of the process, however, appears to show that the product is really a mixture of cerium oxide and carbide. The reduction of ceric oxide by carbon apparently takes place in three stages:—$2CeO_2 + C = Ce_2O_3 + CO$. $Ce_2O_3 + 9C = 2CeC_3 + 3CO$. $CeC_3 = CeC_2 + C$.

No. 6, August 11, 1913.

Quantitative Study of the Absorption of Ultra-violet Rays by Acids of the Ethylenic Series.—Jean Bielecki and Victor Henri.—The ethylene bond increases the absorption power for ultra-violet rays in the ethylenic acids the increase being greater the nearer the double bond is to the carboxyl group. The geometrical isomers, fumaric and maleic acids, and mesaconic and citraconic acids, have different powers of absorption, the *cis* form absorbing less than the *trans* form. From the authors' results the following general law can be enunciated:—With a substance of formula A B C the constant of molecular absorption E is equal to a product *a b c* . . . *a β* . . . in which *a, b, c* are factors corresponding to the different molecular groups A, B, C, and *α, β* . . . are factors which indicate the bonds, configurations, and reciprocal positions of these groups.

Molecular Weight of Sulphuric Anhydride.—H. Giran.—The author has determined the heat of vaporisation L of liquid SO_3, and also the heat of solidification S. Then applying de Forcrand's formula, $\frac{L+S}{T}$ = molecular weight, he concludes that the simple formula SO_3 represents the molecule of the gaseous anhydride at the moment of vaporisation.

γ-Phenyl-oxycrotonic Acid.—J. Bougault.—The more detailed study of the behaviour of γ-phenyl-oxycrotonic acid shows that the formula $C_6H_5.CHOH.CH = CH.CO_2H$ agrees best with its chief reactions, although the evidence in its favour is not absolutely decisive. It is noticeable that the transformation of a-phenyloxycrotonic acid into γ-phenyloxcrotonic acid is limited by the inverse reaction and is reversible.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xlvi., No. 11, 1913.

Preparation of Hexamethylbenzene.—Hans Reckleben and Johannes Scheiber.—When an equimolecular mixture of the vapour of methyl alcohol and acetone is led over heated aluminium oxide large quantities of hexamethylbenzene are obtained. Probably mesitylene is first formed and reacts with the methyl alcohol under the influence of the catalyst. Aromatic hydrocarbons can be methylated in presence of aluminium oxide by the action of methyl alcohol, but the acetone-methyl alcohol mixture gives better yields. Hexamethylbenzene can easily be brominated, but the authors have not ascertained for certain whether the product is the hexabromide.

Action of Methyl Magnesium Iodide on Silicon Hexachloride.—Geoffrey Martin.—If a molecule of methyl magnesium iodide is allowed to act on one molecule of silicon hexachloride in ethereal solution no volatile methyl derivative of Si_2Cl_6 is obtained, but a yellow powder which is insoluble in acids and in organic solvents separates. Its composition is represented by the formula $CH_3.Si_6O_{13}H_9$. One grm. of it when treated with potash solution yields 169 cc. of hydrogen, and probably the molecule contains three pairs of silicon atoms directly united with one another. When the substance is heated to temperatures of from 200°—400° it gives a mixture of hydrogen and methane, yielding finally a silicon compound which contains no carbon.

Autoxidation of Chromous Salts.—Jean Piccard.—In neutral or acid solution chromous salts on autoxidation yield chromic acid as well as chromic salts. Intermediate products of great oxidising power are formed, and are stable for an appreciable time. They can be titrated separately and comprise two oxides, one of which is very unstable while the other is rather more stable. The existence of another oxide, which is not stable for an appreciable time, must be assumed. No formulæ can as yet be definitely ascribed to these oxides, but the first is probably O:Cr.O.O.Cr:O.

MISCELLANEOUS.

Change of Address.—Messrs. Haseltine, Lake, and Co., Patent Agents, announce that their present address is 28, Southampton Buildings, Chancery Lane, W.C., having removed from 7 and 8, Southampton Buildings.

The Chemical Society of the University of Liverpool.—This Society, which celebrates its twenty-first anniversary this session, will hold its Annual Dinner on Saturday, November 29, at the Midland Adelphi Hotel, Liverpool. Full particulars can be obtained from W. M. Inman, Hon. Sec., University, Liverpool.

Faraday Society.—A General Discussion on "The Passivity of Metals" will take place on Wednesday, November 12 next, in the rooms of the Chemical Society, Burlington House, London, W. The meeting will be open to Fellows of the Chemical Society, Members of the Society of Chemical Industry, the Iron and Steel Institute, the Physical Society of London, and the Institute of Metals. Others interested in the subject desirous of being present should apply to the Secretary of the Faraday Society. The President-elect, Sir Robert Hadfield, F.R.S., will preside, and the following provisional programme has been arranged:—Dr. G. Senter will open the Discussion with a general Introduction to the subject; Dr. G. Grube (Dresden) will read a paper on "Some Anodic and Cathodic Retardation Phenomena and their Bearing upon the Theory of Passivity"; Dr. D. Reichinstein (Zürich) will read a paper on "Interpretation of Recent Experiments Bearing on the Problem of the Passivity of Metals"; Mr. H. S. Allen will read a paper on "Photo-electric Activity of Active and Passive Irons." Communications will be read from Prof. Dr. G. Schmidt (Münster); Prof. Dr. Max LeBlanc (Dresden); Prof. Dr. E. Schoch (Texas); Prof. Dr. Günther Schulze (Reichsanrtalt Charlottenburg). The meeting will then be open for general discussion. Sir Robert Hadfield, Dr. J. Newton Friend, Mr. R. N. Lennox, and others will show specimens of non-corrodible metals and alloys. Members desirous of contributing papers to the Discussion or exhibiting any specimens are requested to communicate at once with the Secretary.

MEETINGS FOR THE WEEK.

Thursday, 30th.—Chadwick Public Lectures, 5. (The University, Bristol). "Physiological Principles of Heating and Ventilating," by Dr. Leonard Hill.

Erratum.—P. 188, col. 2, line 3, *for* "irregularities" *read* "regularities."

THE CHEMICAL NEWS

Vol. CVIII., No. 2814.

NEW RESEARCHES ON LIQUID CRYSTALS.*

By O. LEHMANN.

(Concluded from p. 204).

IV. *Swelling up of Liquid Crystals and Myelin Forms.*

If water is continually added to anhydrous neutral ammonium oleate the crystals of this salt disappear, and more and more crystals of the liquid-crystalline neutral ammonium oleate appear until finally they only are present, as has already been shown. At this stage the quantity of water added is just sufficient to convert the anhydrous into the hydrated oleate, and the amount of water contained in the latter can be accurately expressed in numbers, if the mixing is performed on the balance and the result is continually tested by the microscopic examination of small specimens. If the liquid-crystalline hydrate of ammonium oleate thus obtained is placed on a glass plate and rubbed up with more water by means of a spatulum, it is found that (until certain limits are reached) these further quantities of water are completely taken up by the substance. The latter does not change into a paste of liquid crystals and water, *i.e.*, into a heterogeneous mass, but it remains homogeneous, takes up a larger volume and swells up, finally being converted into a more sticky substance, the double refraction of which is smaller for equal thickness (Note 8). In order to prevent the hydrolytic decomposition of the oleate it is better to use ammonia instead of water. The dissolved ammonia has a protective action without having any ill effect, since there is no basic ammonium oleate, so that the ammonia is not taken up by the mass.

Swelling up is generally a process of a chemical nature. Thus the anhydride of calcium sulphate swells up in damp air, forming gypsum, *i.e.*, hydrated calcium sulphate. A solution of the anhydride in water is first formed, and since it is saturated with gypsum the latter crystallises out, then a corresponding fresh quantity of anhydride dissolves, and this process is continued until finally all the anhydride is converted into gypsum. In aqueous solution the swelling up is not seen, because the gypsum dissolves too readily in water. The fact that it can be observed in the case of ammonium oleate is due to the insolubility of the hydrated product resulting from the swelling. It can remain for a long time in contact with a large excess of water, but it gradually forms a colloidal solution (soap water) (see F. Goldschmidt and L. Weissman; *Kolloid-Zeit.*, 1913, xii., 18), the dissolved substance breaking up to form small solid particles in suspension, which can no longer be detected by ordinary microscopical methods. Probably a hydrate with a still larger percentage of water is formed. By the addition of salt (ammonium chloride or bromide, &c.) the process is reversed and a liquid solution, rich in water, is formed, while if no such addition is made the process is irreversible.

R. Virchow was the first to observe these swelling up phenomena in the investigation of animal tissues and parts of the nerve substances (*Arch. Path. Anat.*, 1853, vi., 562, "On the Wide Distribution of a Substance Analogous to Nerve Marrow in Animal Tissues." He compares the process to that occurring when starch is put into warm water; see also O. Lehmann, "Molecularphysik," 1888, i., 546, Sect. 3 and 4). Virchow was of the opinion that they are the characteristic peculiarity of a definite substance formed in the organism, which he called myelin. He did not attempt to find a physical explanation of the peculiar thread and drop-shaped forms resulting from the process; they appeared to him to be a phenomenon necessarily accompanying the swelling up process, and of secondary importance.

F. W. Beneke ("Studien über das Vorkommen, die Verbreitung und die Funktion von Gallenbestandteilen in den thierischen und pflanzlichen Organismen," Giessen, 1862) succeeded in obtaining similar formations by introducing crystals of cholesterin into soap water, and also by adding to pure water the residue obtained by the evaporation of the alcoholic extract of boiled yolk of egg, as Goblez had already observed (after Virchow).

C. Neubauer (*loc. cit.*, 1866, xxxvi., 303) then showed that a definite substance, "myelin," of which these swelling up phenomena were characteristic, does not exist, and that the same "myelin forms" are obtained when pure oleic acid and aqueous ammonia are brought together. Since the latter combines with the oleic acid to form neutral ammonium oleate hydrate, he might have further concluded that this hydrate must give myelin forms when brought into contact with ammonia. He did not make this inference, and the mention of the use of oleic acid led G. Quincke to put forward his theory, recently revived by A. Mlodziejowski (neglecting the fact that the acid is decomposed by ammonia), that the myelin forms consisted of a thick paste of solid ammonium oleate crystals in an envelope of oleic acid, a theory which was proved to be untenable (G. Quincke, *Wied. Ann.*, 1894, liii., 603; see also J. Gad, *Archiv. Phys.*, 1878, p. 181; G. Quincke, *Archiv. Phys.*, 1879, xix., 129; E. Brücke, *Wien. Sitzungsber.*, 1879, iii., 79, 267; Famintzin, *Bull. Acad. St. Petersb.*, 1884, xxix., 414; O. Lehmann, "Molekularphysik, 1888, i., 523). He gives the following summary of it:—"The oleic acid with much alkali and a little water forms at the surface of contact with freshly introduced water thin layers of oleic acid, which rapidly surround either the remaining soap crystals or those freshly formed (neutral or acid alkali salt of oleic acid with water of crystallisation), and form the myelin structures. These myelin forms alter, the liquid oleic acid skin giving up water to the soap crystals. The volume of these soap crystals, which gradually alter and break up, is thus increased. The resulting soap solution periodically exceeds the limits of the oleic acid, and aqueous liquid produces eddies and peculiar movements. This spreading out and the flowing of the liquid may draw out the hollow envelopes of oleic acid filled with soap crystals to form long hollow threads of oleic acid, filled with sticky masses or soap crystals. In consequence of the surface tension at the bounding surface of the oleic acid and surrounding liquid these threads of oleic acid collect together and form hollow balls or bubbles. These hollow bubbles filled with aqueous soap solution or sticky masses of soap are displaced by the periodic spreading out of the soap solution at the surface of the skin of oleic acid, both in the surrounding aqueous liquid and also along the hollow threads of oleic acid, and run together to form one or more larger hollow balls or bubbles." I was at first misled by these statements, because I thought I had observed phenomena which confirmed them. In particular I thought I could demonstrate the existence of a skin of oleic acid and of differences of surface tension which might cause the formation of the peculiar forms, although I had already realised that it was not a question of solid but only of liquid (or, at any rate, fluid) ammonium oleate crystals. From my continued experiments (with other substances also) I gradually came to the conclusion that Quincke's theory is untenable, is due to different optical illusions, and gives no explanation of the phenomena (*Wied. Ann.*, 1895, lvi., 771; *Ann. Phys.*, xix., 22, 407; 1906, xx., 63; "Die scheinbar lebenden Kristalle," Esslingen, 1907; *Biolog. Zentralbl.*, 1908, p. 481; "Die neue Welt der flüssigen Kristalle," 1911, p. 264). The hypothetical oleic acid envelope of the myelin forms does not exist, and thus there is no question of differences of surface tension. The myelin forms are only

* Abridged from *Sitzungsberichte der Heidelberger Akademie der Wissenschaftung*, 1913, A, xiii.

liquid crystals of peculiar molecular structure. Their surface tension is the same at all places, and their formation is due to the action of the same shaping force which, in conjunction with alterations of surface tension owing to swelling up, determines the shape of liquid crystals (Note 9). In any case it cannot be directly deduced from the known facts that we are dealing with forces which are not known in Physics, and the study of which will probably explain many actions which cannot be understood from a physical point of view, but which come into play in the organic kingdom; for the myelin forms and the apparently living crystals allied to them are the only lifeless structures which exhibit close analogies to the organism, which consists of the same molecules as lifeless substances

The normal liquid crystals of neutral ammonium oleate hydrate are converted continuously into the myelin forms, although the water is taken up only in stochiometric proportions, *i.e.*, by definite amounts. If we assume that besides the hydrate existing in the form of normal liquid crystals only one other richer in water can exist, its composition being given by the greatest amount of water which the liquid crystals can take up, we can explain the steady transition by supposing that the two liquid-crystalline hydrates can form mixtures in all proportions, and that these mixed crystals appear more liquid and show less deviation of the rays resulting from double refraction for equal thickness, the more they contain of the hydrate which is richer in water.

If continually increasing quantities of water, or better still (for reasons already stated) aqueous ammonia, are added to a solution of the normal liquid-crystalline mass in alcohol, the corners become more and more rounded off while the individual crystals get shorter. If the crystals were originally scarcely visible in ordinary light because their indices of refraction were nearly the same as that of the mother-liquor, as the quantity of water in the solution increases their outlines become more distinct, so that it is not necessary to use crossed Nicols in order to see them. Their extinction between the latter finally becomes abnormal, fan structures being formed at various places, probably because the leaflet-shaped molecules endeavour to arrange themselves parallel to the curved surface. If the chrysalis form changes into the spherical form the structure becomes perfectly sphaerolithic; the spheres in every position between crossed Nicols show the black cross of sphaero-crystals (Note 10).

This molecular structure, *i.e.*, the arrangement of the molecular leaflets parallel to the surface, the optical axis being everywhere perpendicular to the latter, is characteristic of the myelin forms, which are to a certain extent liquid sphaero-crystals drawn out to form little rods. Occasionally, but by no means invariably, they are hollow, *i.e.*, the liquid-crystalline mass appears as a crust on a central part formed of isotropic liquid mother-liquor. The orientation of the molecules is then the result of the influence of the outer as well as the inner surface. In most cases the hollowness is only an illusion produced because the water contained in the mass alters by leaps and bounds from the interior outwards, or because the structures are on glass and at the places in question, like other liquid crystals, become semi-isotropic, and thus appear dark between crossed Nicols. The structure of myelin forms can be seen best if the alcoholic solution of the ammonium oleate, in which isolated liquid crystals have separated, is placed under a cover-glass shaped like a watch glass (concave side upwards), and ammonia is allowed to flow round it. In consequence of the contact movement the alcoholic solution makes arch-shaped incursions into the ammonia, and vigorous mixing of the two liquids takes place owing to diffusion. Just at the boundary the alcoholic solution which has diffused into the ammonia may persist. But as it presses forward and mixes more with water the ammonium oleate is precipitated in the form of very small chrysalis-like liquid crystals. There are only a few of them, as the solution mixes with ammonia only with difficulty. Conversely the ammonia penetrates into the arching parts of the alcoholic solution, and causes the formation of a precipitate of liquid crystals which unite to form a semi-isotropic crust, all the molecular axes arranging themselves perpendicularly to the surface. Thus the beginning of a kind of hollow myelin formation results, the interior being filled with alcoholic mother liquor. As the diffused water penetrates further, which is furthered by the formation of currents in consequence of contact movements, the myelin forms separate as drops which are surrounded with a liquid-crystalline skin. Numbers of such drops run together to form a frothy mass, the frothy walls of which are semi-isotropic liquid crystalline lamellæ, while the inside of the cells consists essentially of aqueous soap solution.

If instead of the alcoholic solution pure liquid crystalline ammonium oleate hydrate is used the same diffusion processes take place, but they are confined to the immediate neighbourhood of the limiting surface, and are only manifested by the effect that hydrate richer in water is formed there and continually goes over into that already present. At places where by the adsorption power of the glass this hydrate possesses semi-isotropic structure, so that the principal axes (optical axes) of the molecules are perpendicular to the surface of the glass, the same also holds good for the hydrate richer in water. The so-called oily streaks clearly appearing between crossed Nicols go continuously over into the likewise bright looking margins of the myelin forms (see "Die neue Welt der flüssigen Kristalle," 1911, p. 196; this can be seen very well on the addition of eosin, when the formation of myelin forms is very incomplete). Owing to the formation of this hydrate the consistency of the mass as well as its surface tension becomes very small at the places in question, and as the volume is increased owing to the absorption of water the projections known as "myelin forms" result. The fact that they take the form of a cylinder, and the diameter of the cylinder remains the same when further swelling up occurs, is explained by the difference of the surface tensions of the swollen and unswollen parts which always remain the same. My earlier statements (*Wied. Ann.*, 1895, lvi., 780) must thus be corrected, difference of surface tension between soap and oleic acid being replaced by that between swollen and unswollen parts. The pressing out of the snake-like apparently living crystals of para-azoxycinnamic acid ethyl ester (*Ann. Phys.*, 1906, xix., 24, Figs. 26—29) may be explained by supposing that monobromonaphthalin is more readily taken up at the flattened parts of the spheres. It may also be explained by the shaping force of the liquid crystals, the molecules of which endeavour to assume a sphaerolithic arrangement, but owing to the continued swelling up of the mass a cylinder with equal diameter and the same radical structure attaches itself to the hemisphere originally formed. The leaflet-shaped molecules are grouped in concentric circles about the axis just as in the sphaerolithic arrangement they are grouped in concentric spherical surfaces about the mid-point.

When the myelin forms come in contact with the glass both above and below them the molecular axes arrange themselves perpendicularly to the latter. Where the mass touches the glass it becomes semi-isotropic and thus appears dark between crossed Nicols; the walls only in section exhibit fan structure, as I have stated before (*Wied. Ann.*, 1895, lvi., 786, Fig. 19). It is therefore easy to be deluded into thinking that one is dealing with bubbles filled with isotropic liquid. With larger specimens, such as are formed when alcohol is added to the ammonium oleate, or if ammonium linoleate, which forms analogous liquid crystals as well as myelin forms is added, one can recognise in this apparently isotropic liquid "oily streaks" and "conical alterations of structure," which clearly show the nature of the interior of the myelin forms. After taking away the cover-glass by teasing with a mounted needle it may be proved that the interior has actually a gelatinous (or sticky) consistency. The expression is not quite correct, for a jelly is a heterogeneous substance of a

spongy or frothy nature, which in consequence of the presence of solid threads or lamellæ, or on account of the surface tension of the cell walls of the froth, shows a kind of perfect elasticity. The similar phenomenon appearing in the case of the myelin forms, that the mass after teasing endeavours to reassume its original form, and therefore appears gelatinous, on the other hand depends upon another cause, namely, the shaping force of the liquid crystals which conditions the shape of the myelin forms and differs both from elasticity and from surface tension, although, as has been said above, it is to be regarded as the effect of molecular forces.

As at least two different hydrates of ammonium oleate are concerned in the mixing it would be expected, as in other cases of the formation of mixed crystals of non-isomorphous substances (*Zeit. Kristallog.*, 1877, i., 483, 528; 1883, viii., 433; *Zeit. Phys. Chem.*, 1887, i., 15; 1891, viii., 543; *Wied. Ann.*, 1894, li., 47; "Flüssige Kristalle," 1904, pp. 150—182; "Die scheinb. lebl., Krist., 1907, p. 52; "Die neue Welt der flüssigen Kristalle," 1911, p. 122; *Verh. d. Karlsr. Nat. Ver.*, 1913, xxv.), that the structure of the myelin forms would show deviations from the normal structure just as the structure of crystal drops suffers spiral distortion owing to the presence of foreign substances, the distortion manifesting itself in the efforts of the drops to rotate, in rotation of the plane of polarisation, &c. (*Ann. Phys.*, 1900, ii., 649. 687; 1905, xviii., 808; "Flüssige Kristalle," 1904, pp. 28—34, Tables XIV.—XVII.; *Phys. Zeit.*, 1911, xii., 540; *Ann. Phys.*, 1911, xxxv., 193; *Heidelb. Sitzungsber.*, 1911, No. 22, Tables VI.—VIII.; 1912, No. 13, Table III.; Fig. 64; *Ann. Phys.*, 1912, xxxix., 105). As a matter of fact the myelin forms show a tendency to rotate, the result of which is that if a cylindrical thread cannot turn freely, for instance, because the end is twisted and touches the glass, or because it has run into the swelling mass, the one part of the thread twists round the other or they both form a double spiral.

The supposition that the myelin forms are of the nature of mixed crystals is confirmed by their frequently stratified structure, which can be explained only by a difference in the character of the deposited layers. As these layers have everywhere the same thickness, although the myelin form steadily grows, it follows that the later layers are not simply deposited on the former, as in ordinary stratified mixed crystals, but that the structure grows by interpenetration of water molecules (swelling up), just as the growth of an organism is due not to apposition but to intussusception. Even foreign substances can be taken up in the myelin forms, but they possess the same power of self purification as other crystals (*Zeit. Kristallogr.*, 1877, i., 487; "Molekular-physik," 1888, i., 345; "Flüssige Kristalle," 1904, p. 137; "Die neue Welt der flüssigen Kristalle," 1911, p. 330; *Phys. Zeit.*, 1910, xi., 44; *Umschau*, 1910, xiv., 950). Thus, for example, if different aniline colours are added to the ammonium oleate or ammonia, the myelin forms do not take up the colour. Prepared myelin forms only become a faint blue very slowly in an ammoniacal solution of methylene blue, even if the concentration of the dye is very high. But if they are formed in such a solution they acquire an intense pure blue colour, while the solution is decolorised. (The colour of the solution is more violet than blue). Probably a new compound is formed which can only slightly diffuse into the liquid crystals, or not at all, but which can be deposited to a considerable extent if it is firmly bound by the adsorption power during the growth of the crystal. The effect is even more striking if in the preparation of myelin forms instead of pure ammonia the almost colourless solution of gentian violet in ammonia is used. The freshly formed myelin forms become deep violet, although both solutions, in the mixed zone of which they appear, are colourless. As the formation of the myelin forms is only a little influenced by the addition of dyes, their use is to be recommended for demonstrations of the phenomena, for the intensely coloured structures stand up well against the colourless ground (Note 11).

To a certain extent the myelin forms can absorb ammonium ricinoleate, which gives the same liquid crystals as oleic and linoleic acids. The formation of myelin forms ceases, however, when the percentage is large, as would be expected, for ammonium ricinoleate cannot yield myelin forms of itself, probably because it is too readily soluble in aqueous ammonia.

On projection the myelin forms always appear yellowish on a white ground. There seems to be a sort of dissipation of light as in the Tyndall effect, which must be caused by the deviation of the molecules from parallelism.

When the action of the water (or, better still, ammonia) is continued, the arrangement of the molecules in myelin forms is finally lost, and they disappear, giving, as has been already said, a soap solution. By the addition of salts (ammonium chloride or bromide) and some alcohol, chrysalis-like structures can be precipitated from such solutions; these must be regarded as hollow liquid crystals, the interior of which is filled with isotropic liquid. First of all droplets of concentrated oleate solution separate out, and on their surfaces, in consequence of continued electrolytic action, a semi-isotropic liquid-crystalline skin is formed. By the flowing together of such hollow sphaerocrystals complicated structures result, which like masses of froth are divided internally into several divisions by plane (liquid crystalline) lamellæ (Note 12).

The swelling up of liquid crystals recalls the swelling up of starch grains, which show a black cross between mixed crystals, and are thus probably sphaerolithic formations (*cf.*, on the other hand, G. Malfitano and A. Moschikoff, *Comptes Rendus*, 1913, clvi., 1412) or crystals of white of egg (Schimper, *Zeit. Kristallog.*, 1881, v., 131; St. Bondzynski and L. Zoja, *Zeit. Phys. Chem.*, 1894, xix., 1; A. Wichmann, *Ibid.*, 1899, xxvii., 575), which can take on an intense coloration, or hæmoglobin crystals (A. Rollet, *Sitzungsber. der Wiener Akad.*, 1862, [2], xlvi., 65). The absorption of foreign substances by zeoliths and other solid crystals (F. Rinne, "Fortschritte der Mineralogie, Kristallographie, und Petrographie," 1913, iii., 159) may be an allied phenomenon, as also the migration of silver ions in silver iodide crystals (O. Lehmann, *Wied. Ann.*, 1889, xxxviii., 396) and the artificial coloration of crystals by radium rays (C. Doelter, "Das Radium und die Farben," Dresden, 1910), phenomena which show that the structure of crystals can be obtained by the molecular directive force, in spite of the loosening influence of thermic motion. Since new molecules are obtained by the puffing up, the preservation of the structure must be due to the fact that the new molecules are regularly arranged in consequence of the molecular directive force, as in polymorphic changes (*Zeit. Kristallogr.*, 1877, i., 107), and the solution of hydrated salts (*loc. cit.*, p. 102, Table V., Figs. 1—4). We are forced to the conclusion that the diffusion of water does not take place under the influence of osmotic pressure as the theory of "solid solutions" assumes, *i.e.*, by the interpenetration of molecules of water between the molecules of crystals, but (as in the migration of ions) from molecule to molecule, in such a way that molecules at the surface which have taken up water give it up to inner molecules containing less water, and that it is then similarly passed on to molecules which are still further in and are poorer in water. Swelling up thus consists in continual dissociation and reproduction of molecules containing water, according to the law of mass action.

Notes.

8. The displacement of the rays seems to be the same for equal amounts of the original substance.

9. The experiment which I brought forward in favour of the influence of oleic acid was faulty (*Wied. Ann.*, 1894 lvi., 776, Fig. 2). Apparently an accidental current in the liquid produced the opposite effect to that which ought to have been seen. The myelin forms hardly appear, or are altogether absent where there is free oleic acid, but are very abundant where no oleic acid is present. To a

very small extent they result from acid ammonium oleate, and then only because some neutral oleate is formed by contact with water.

10. Specially fine crystals of this kind can be obtained by cooling hot solutions of cholesterin with cetyl alcohol or elaidinic acid in a very little alcohol. As they separate they fall into a state of rapid motion, which is due to the local change of composition of the solution caused by the separation; this change of composition leads to differences of surface tension, and hence contact movement like that of camphor on water. It recalls the Brownian molecular movement. During the formation of myelin forms in water, when growth and solution continually alternate, sometimes violent movements which have the same origin occur.

11. G. Quincke (*loc. cit.*) has also observed the absorption of methylene blue, but he ascribes it to the hypothetical envelope of oleic acid, as oleic acid takes up the colour from aqueous solutions.

12. In some cases I also obtained comma shaped structures, club-shaped at one end, and diminishing by degrees towards the other. I could not determine the conditions with great accuracy, but they seemed to be myelin forms, the structure of which is greatly altered by the presence of foreign substances. They appeared in a commercial gelatinous ammonium oleate which with ammonia alone gave no myelin forms, but only on addition of salt.

THE ATOMIC WEIGHT OF TELLURIUM, AND A CRITIQUE OF THE BASIC NITRATE METHOD OF DETERMINATION.

By WM. L. DUDLEY and PAUL C. BOWERS.

THIS work is a continuation of the investigation of tellurium, begun by Dudley and Jones, who made a spectrographic study of it (*Journ. Am. Chem. Soc.*, xxxiv., 995). Our object, in the beginning, was to make atomic weight determinations of different fractions of tellurium precipitated by hydrazine hydrochloride, and thus to confirm the conclusions reached by Dudley and Jones, that tellurium did not suffer decomposition when so treated; but later it was found desirable to make an investigation of the basic nitrate method for determining the atomic weight.

The tellurium used in this investigation was purified as described by Dudley and Jones (*loc. cit.*) There were in all twenty fractions of the tellurium, about 6 grms. to the fraction, precipitated by hydrazine hydrochloride. The spectrograms taken of the different fractions showed no impurities, with the exception of the last one.

Unless otherwise stated Kahlbaum's chemically pure reagents were used. Ammonia-free water was used for all dilutions.

Very concordant results have been obtained by Köthner (*Ann.*, cccxix., 1), Norris (*Journ. Am. Chem. Soc.*, xxviii., 1675), and Flint (*Am. Journ. Sci.*, [4], xxx., 209) with the basic nitrate method. Therefore we began the work by using this method. Our procedure was as follows:—The tellurium was dissolved in nitric acid (sp. gr. 1·25), and evaporated on a steam-bath at about 70°. The basic nitrate which crystallised out was washed with concentrated nitric acid, and then dried by heating at 120° in a current of air dried by sulphuric acid and phosphorus pentoxide. These crystals were then ground in an agate mortar. Portions were weighed in a platinum crucible, and brought to constant weight by heating in a current of dry air at a temperature of 140° for periods of twenty-four hours each. The crucible was then placed over a low Bunsen flame, and the temperature very slowly and gradually raised to the fusion-point of the dioxide.

A Freas electric oven was used for drying the crystals and bringing the basic nitrate to constant weight. This oven was regulated to vary only a fraction of a degree. In order to draw the air over the basic nitrate, a specially constructed glass apparatus was made to fit into the oven.

The fractions Nos. 1 and 2, when dissolved in nitric acid, gave to all appearances the orthorhombic crystals of the basic nitrate, but from the solution of the third fraction, there separated colourless crystals of perfect octahedral form. These proved to be crystals of tellurium dioxide. They dissolved with difficulty in a large excess of nitric acid (sp. gr. 1·25). But from this nitric acid solution of the dioxide there would usually separate, on concentration, the orthorhombic crystals of the basic nitrate, but sometimes it would separate as the dioxide again.

Thinking that there might be some difference between the tellurium which came down in the octahedral form as the dioxide and that crystallising in the orthorhombic form as the basic nitrate, samples of the two were reduced to the elementary state (tellurium), and spectrograms were taken of each. A comparison of the spectra was made but no difference was noted. In order to be sure of this point, it was decided to make atomic weight determinations of them, so whenever the dioxide crystals appeared they were separated from the liquid by decantation, washed with concentrated nitric acid, dissolved in nitric acid, sp. gr. 1·25, and the solution evaporated until the orthorhombic crystals separated. Sometimes the dioxide crystals would again appear on concentration, as previously mentioned. These were treated with more nitric acid (sp. gr. 1·25), and the operation repeated until only the crystals of the basic nitrate form were obtained. In fraction No. 15 especial effort was made to avoid the formation of any dioxide crystals, by dissolving in a very large excess of acid. Then only the orthorhombic crystals were obtained from the solution, but they were found to contain inclusions of the dioxide.

As the amount of basic nitrate obtained from the different fractions was not enough for a series of atomic weight determinations, the crystals of the fractions Nos. 1, 2, 3, and 4, and Nos. 5, 6, 7, and 8, &c., first separating in the orthorhombic form were put together, ~~and the~~ crystals of the dioxide which were converted into the basic nitrate were grouped in like manner.

Portion.	Fraction Nos.	Det. No.	$2TeO_2HNO_3$. Grms.	TeO_2. Grms.	TeO_2. Per cent.	Atomic wt.
A	1, 2, 3, and 4	1	1·74464	1·46204	83·796	130·94
A	1, 2, 3, and 4	2	1·08072	0·90445	83·689	129·65
A	1, 2, 3, and 4	3	1·93538	1·61476	83·434	126·69
A	1, 2, 3, and 4	4	1·34715	1·60841	83·750	130·39
A	1, 2, 3, and 4	5	1·33704	1·59490	83·832	131·37
A	5, 6, 7, and 8	6	2·27174	1·91397	84·251	136·56
A	5, 6, 7, and 8	7	1·61049	1·35653	84·230	136·61
A	5, 6, 7, and 8	8	1·67029	1·40286	83·976	133·13
B	1, 2, 3, and 4	9	1·55380	1·38070	83·391	126·13
B	1, 2, 3, and 4	10	1·26647	1·05595	83·377	126·04
B	5, 6, 7, and 8	11	1·74197	1·45398	83·455	126·93
B	5, 6, 7, and 8	12	1·19549	0·99758	83·428	126·62
B	11 and 12	13	0·59279	0·49295	83·157	123·58
B	11 and 12	14	0·60778	0·50670	83·396	125·95
B	15	15	1·62585	1·39745	85·952	160·78
B	15	16	1·28903	1·09327	84·813	143·96

The preceding are the results obtained. For convenience of tabulation, the determinations of the portions first crystallising as the dioxide are marked "A" and those separating from the original solution in the orthorhombic crystals of the basic nitrate, "B."

In all of the atomic weight determinations the weighing was made by the method of oscillations. The set of weights used was standardised, and the weighings were reduced to vacuum.

As the results were so irregular the method was necessarily abandoned. According to our experience there is no certainty of the purity of the basic nitrate crystals. From a nitric acid solution the tellurium may crystallise

as tellurous acid, tellurium dioxide, and the basic nitrate of tellurium according to the temperature and excess of acid present. Thus the conditions for crystallisation must be very exact in order to obtain pure crystals of either. What all of these conditions are we are not prepared to say. The temperature may be regulated and before evaporation a large excess of acid may be present; but on concentrating the solution it often becomes supersaturated, and there is not sufficient nitric acid present to form the basic nitrate with all of the tellurium. So the dioxide either crystallises out or is held as an inclusion in the orthorhombic crystals of the basic nitrate. Such inclusions were observed on close examination with the microscope. Also when the dioxide and basic nitrate are together, some of the dioxide is always held between the basic nitrate crystals, which have a tendency to form rosette clusters. This tends toward high results, and with one exception determinations marked "A" gave high results. The crystals from the solution of fraction "B," No. 15, also contained these inclusions. Although, as said above, only orthorhombic crystals separated from this solution, still they gave the highest results, owing to the amount of dioxide included.

In all of the determinations marked "B" in which the basic nitrate was crystallised out after the dioxide crystals had been separated from the solution, low results were obtained. These low results were due to inclusions of the mother-liquor, instead of the dioxide, as in the case of high results. These inclusions were also observed under the microscope. Baker and Harcourt (*Journ. Chem. Soc.*, xcix., 1311) conclude from their investigations that some of the trioxide basic nitrate may be formed in small amounts along with the dioxide basic nitrate of tellurium, and in this way they attempt to account for the low results of Flint.

That some of the dioxide may be lost mechanically by the gases evolved when the nitrate is decomposed by heating should also be taken into consideration. But only in one or two instances was there any evidence of this on the lid of the crucible, and these determinations were discarded. Then there is the uncertainty as to whether all the oxides of nitrogen are driven off at the fusion-point of the dioxide. For all of the reasons given above we have come to the conclusion that this method is not dependable.

The Tetrabromide Method.

Owing to the failure of the basic nitrate method to give reliable results, we adopted the tetrabromide method for determining the atomic weight of the fractionally precipitated tellurium. The tetrabromide method presented by Baker and Bennett (*Journ. Chem. Soc.*, xci., 1849) is very simple, and avoids the danger of loss due to transferring of material from one vessel to another, and the authors got exceedingly concordant results.

Baker's "Analysed Bromine" containing from 0·26 to 0·46 per cent of chlorine was purified according to the method given by Stas. A pound of bromine was distilled over chemically pure zinc oxide and potassium bromide, ten times the amount of each required for the chlorine present being used. The bromine was then treated with phosphorus pentoxide in a separatory funnel, and allowed to stand for several hours. Finally, the bromine was drawn off and re distilled.

Each fraction of the tellurium which had been converted into the basic nitrate for the previous method was twice evaporated to dryness with hydrochloric acid, then dissolved in hydrochloric acid, diluted to the precipitating point of the tellurium dioxide with ammonia-free water, and sulphur dioxide passed into the hot solution. The tellurium thus precipitated was filtered through hardened filter-paper, washed first with hydrochloric acid, 1 : 1, then warm hydrochloric acid, 1 : 4, ammonia free water until free of the chloride, and finally alcohol followed by ether. This was dried in a vacuum over sulphuric acid in order to avoid oxidation of the finely-divided particles of tellurium. More sulphur dioxide was passed into the filtrate, and the process repeated until all of the tellurium was precipitated. The dried precipitated tellurium was then fused into sticks, after the method used by Dudley and Jones (*loc. cit.*), for the preparation of electrodes.

Portions of this fused tellurium were powdered in an agate mortar, and placed in the lower bulb of the weighed tube, which was specially constructed of Jena glass according to the diagram given by Baker and Bennett (*Journ. Chem. Soc.*, xci., 1857). This was dried to constant weight by heating in the electric oven at 50° in a current of air dried by calcium chloride, sulphuric acid, and phosphorus pentoxide. The air was then displaced by nitrogen. The nitrogen was obtained by passing air over red-hot copper turnings, then through a potassium hydroxide solution of pyrogallic acid, and was dried in the same way as the air. The purified bromine was run into the upper bulb of the tube through a funnel with a drawn-out stem, and then the tube was tightly capped. The bromine was run down into the tellurium a little at a time, until the tellurium was all converted into the tetrabromide, and some excess of liquid bromine remained. This was allowed to stand for about twenty-four hours. The tube was then placed in the electric oven, and heated to 50°, while a current of dry nitrogen was drawn through it. When no tests for bromine with potassium-iodide starch paper was obtained in the nitrogen drawn through the tube, the oven was allowed to cool to room temperature. The nitrogen was then displaced by dry air and the tube weighed. A similar tube was used as a counterpoise.

Concordant results were not obtained from the tellurium precipitated and cast in sticks as described. Notwithstanding washing with hydrochloric acid, drying in a vacuum, and fusion in hydrogen, the tellurium contained some dioxide, and, as was discovered later, some impurities. Parts of the series 1, 2, 3, and 4; 5, 6, 7, and 8; 11 and 12, A and B were put together, and distilled in hydrogen. A residue of about 0·1 per cent was left in the boat. This residue was found to contain some carbon, which was very probably due to the hydrogen, although it was generated from chemically pure zinc and hydrochloric acid; a slight trace of iron which must have come from the can of liquid sulphur dioxide, as no iron lines were previously found in the spectra of the tellurium; some tellurium and microscopic fragments of glass, due to shattering the glass tube to remove the fused tellurium. This tellurium, when re-distilled, left only a slight coloration in the boat, showing that the one re-distillation was sufficient to purify the material. The results of the determinations are as follows:—Br = 79·92.

	Wt. of Te. Grm.	Wt. of $TeBr_4$. Grms.	Te in $TeBr_4$. Per cent.	At. wt. of Te.
No. 1	0·479816	1·682387	28·520	127·550
No. 2	0·296341	1·037049	28·575	127·897
No. 3	0·433241	1·516746	28·563	127 819
No. 4	0·457782	1·605684	28·510	127·487
No. 5	0·321522	1·126939	28·530	127·612

The high results in these determinations were due to some tellurium which was left in the bulb unattacked by the bromine. This was caused by running the bromine into the lower bulb too rapidly; thus inclusions of tellurium were formed in the tellurium tetrabromide which could not be broken up by shaking the tube. It is best to start with smaller quantities of tellurium than those used above, because it allows better mixing of the material, and thus brings the bromine into contact with all of the tellurium.

The remainder of the portions "A," Fractions Nos. 1, 2, 3, and 4, "B." Fractions, 1, 2, 3, and 4, also the Fraction No. 19 of the tellurium precipitated by hydrazine hydrochloride were distilled separately in hydrogen, and the atomic weight determinations gave the following:—

Fraction Nos.	Det. No.	Wt of Te. Grm.	Wt. of $TeBr_4$. Grms.	Per cent of Te.	At. wt. of Te.
A 1, 2, 3, and 4	1	0·300558	1·054251	28·509	127·481
A 1, 2, 3, and 4	2	0·199807	0·700947	28·505	127·456
B 1, 2, 3, and 4	1	0·22032	0·773048	28·500	127·425
B 1, 2, 3, and 4	2	0·158161	0·554717	28·512	127·500
19	1	0·436907	1·532360	28·512	127·500
19	2	0·29811	1·045485	28·514	127·512
			Average	28·509	127·479

These determinations show that there is no separation of the tellurium after 19 fractional precipitations by hydrazine hydrochloride, and that there is no difference between the tellurium which crystallised from the nitric acid solution in the octahedral crystals as the dioxide and that separating in the orthorhombic crystals as the basic nitrate.—*Journal of the American Chemical Society*, xxxv., No. 7.

A STUDY OF THE METALLIC TELLURITES.*

By VICTOR LENHER and EDWARD WOLESENSKY.

(Concluded from p. 206).

Magnesium Tellurite.—This substance was obtained from a solution of magnesium chloride by adding a solution of sodium tellurite. It is a white flocculent precipitate, which is slightly soluble in water. On standing for a time in the mother-liquor or in water, it becomes granular and heavy. The composition of the precipitate is not affected by varying the proportion of the two salts from which it is formed.

This tellurite was found to have the composition $5MgTeO_3.9H_2O$.

Calculated.—Mg, 10·84; Te, 54·91; H_2O, 13·94.
Found I.—Mg, 9·98; Te, 55·29; H_2O, 13·48.
Found II.—Mg, —; Te, 54·91; H_2O, 13·62.
Found III.—Mg, 9·91; Te, 55·39; H_2O, 13·65.
Found IV.—Mg, 9·70; Te, 55·10; H_2O, 14·29.
Found V.—Mg, 9·93; Te, 55·59; H_2O, 13·36.

In the above table, numbers I., II., and III. were precipitated from solutions containing excess of sodium tellurite, while IV. and V. were precipitated from solutions containing an excess of magnesium chloride.

Owing to the somewhat unusual ratio of the water to magnesium tellurite in this compound, a more careful study was made of this relation. A quantity of the dried precipitate, equivalent to 1 grm. of anhydrous tellurite, was heated at various temperatures until the weight became constant. Then, from the total water content and the loss in weight at each temperature, it was possible to calculate the amount of water still retained.

Temp.	H_2O held by 1 g. $MgTeO_3$.	Temp.	H_2O held by 1 g. $MgTeO_3$.
20°	0·1545	260°	0·0758
100°	0·1360	300°	0·0250
130°	0·1170	330°	0·0130
175°	0·0965	360°	0·0080
200°	0·0860	400°	0·0050
220°	0·0838	450°	None

If these results are plotted in a curve it will be seen that at about 260° there is a sharp break in the curve, and that the amount of water retained at this temperature is very nearly one-half of the original amount, 0·1545 grm. Above this temperature there is a rapid falling off in the water content, until at 450° all the water can be driven off in fifteen minutes.

This experiment indicates that between 450° and ordinary temperature, there exist at least two definite hydrates of magnesium tellurite, namely, $5MgTeO_3.9H_2O$, and $10MgTeO_3.9H_2O$. It might also be noted that the composition at 100°, as calculated from the above results, is $2MgTeO_3.3H_2O$ although this may have no special significance, since no data were obtained for temperatures below 100°. It is also quite evident that most of the water in this compound is quite firmly held.

Barium Tellurite.—To obtain this substance, a solution of sodium tellurite was added to a solution of barium chloride. A white flocculent precipitate was obtained, which was only slightly soluble in water. Attempts were made to obtain barium tellurite in crystalline form but were unsuccessful. Analysis of different samples showed a considerable variation in composition. Investigation showed that the precipitates always contained barium chloride, and sometimes in considerable quantities. This barium chloride could not be washed out completely by repeated and long-continued boiling with large quantities of water. Accordingly the precipitation was performed in dilute solutions, containing exactly equivalent quantities of the two salts. Even under these conditions the precipitates always contained small amounts of barium chloride which could not be washed out.

The analysis of this substance was carried out in the following way. Water was determined as usual. The chlorine was determined by precipitation with silver nitrate, from a nitric acid solution of the barium tellurite.

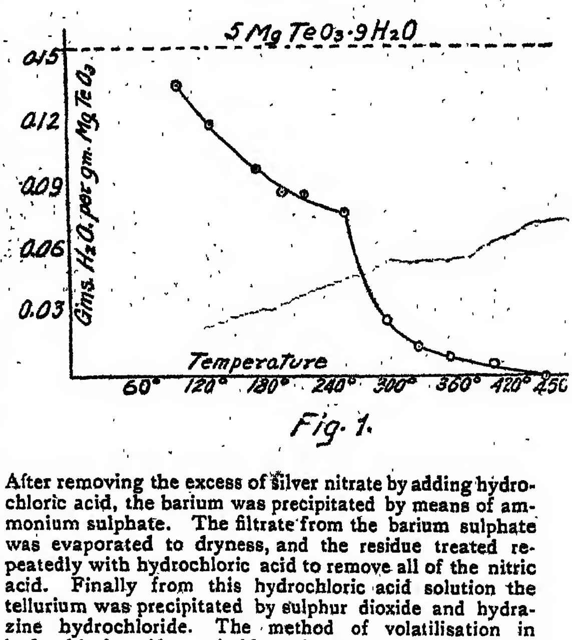


Fig. 1.

After removing the excess of silver nitrate by adding hydrochloric acid, the barium was precipitated by means of ammonium sulphate. The filtrate from the barium sulphate was evaporated to dryness, and the residue treated repeatedly with hydrochloric acid to remove all of the nitric acid. Finally from this hydrochloric acid solution the tellurium was precipitated by sulphur dioxide and hydrazine hydrochloride. The method of volatilisation in hydrochloric acid gas could not be used in this case, since all of the tellurium could not be driven off without raising the temperature so high that barium chloride would volatilise.

The proportion of barium to tellurium was greater than the normal salt should have. But in all cases the precipitates also contained chlorine in appreciable quantities. If the chlorine contained be calculated as barium chloride, and the tellurium as normal barium tellurite, the results agree with the analysis obtained. This is particularly evident in those samples which were precipitated in presence of excess of barium chloride.

Several samples were analysed, in all of which the proportions of barium chloride, tellurite, and water varied considerably. The following analyses are typical examples. The first sample was precipitated in presence of excess of barium chloride; the second one from equivalent quantities of this salt and sodium tellurite.

* *Journal of the American Chemical Society*, xxxv., No. 6.

1. Calculated for $8BaTeO_3 5BaCl_2 4H_2O$.—Ba, 49·50; Te, 28·29; Cl, 9·82; H_2O, 1·99.
Found.—Ba, 48·68; Te, 29·23; Cl, 9·43; H_2O, 190.
2. Calculated for $20BaTeO_3 \frac{1}{2}BaCl_2 20H_2O$.—Ba, 41·89. Te, 37·95; Cl, 0·53; H_2O, 5·35.
Found.—Ba, 41·83; Te, 38·33; Cl, 0·53; H_2O, 5·07.

Cadmium Tellurite.—This salt was obtained as a white amorphous insoluble precipitate, by the interaction of cadmium chloride and sodium tellurite.

In its analysis the method of volatilisation could not be used for the separation of the tellurium, on account of the volatility of cadmium chloride. The tellurium was therefore first precipitated from a hydrochloric acid solution of the material by means of sulphur dioxide and hydrazine hydrochloride. In the filtrate from the tellurium, the cadmium was determined in one of two ways. (1) The solution was evaporated to dryness, the residue taken up in water, and the cadmium precipitated as carbonate by means of potassium carbonate, and weighed as oxide. (2) The solution was first neutralised with potassium hydroxide, and potassium cyanide was added until the precipitate first formed just dissolved. This solution was then electrolysed, using a current density of 0·5 to 0·8 amperes per 100 sq. cm., with about 4 to 4·5 volts. After five hours the voltage was increased to 5 volts for an hour.

The composition found did not agree with the normal tellurite. The tellurium was always slightly high and the cadmium correspondingly low. The following gives the average composition found, together with the calculated results for $3CdTeO_3.2H_2O$.

Calculated.—Cd, 37·47; Te, 42·53; H_2O, 4·00.
Found.—Cd, 36·09; Te, 44·20; H_2O, 3·67.

The regular discrepancies appearing in the analysis are explained by the fact that when tellurium is precipitated in the presence of cadmium, it carries down some of the cadmium with it. This is made quite evident from the following experiments.

I. Some tellurium which had been precipitated in the presence of cadmium was dissolved in aqua regia and the solution evaporated to dryness. The residue was then taken up in dilute hydrochloric acid and precipitated by means of hydrogen sulphide. This precipitate was digested for several hours in a warm place with yellow ammonium sulphide. The residue left by the ammonium sulphide was treated with hot concentrated hydrochloric acid and filtered. After nearly neutralising the filtrate with potassium hydroxide, it was treated with hydrogen sulphide. A small amount of cadmium sulphide was obtained.

II. A weighed amount of pure tellurium dioxide was mixed with cadmium chloride (about 0·8 grm.). After dissolving in hydrochloric acid, the tellurium was precipitated with sulphur dioxide and hydrazine hydrochloride. The following results were obtained:—

Te found.—0·7037.	Calculated.—0·6929.
„ 0·9476.	„ 0·8754.

It will be noted that the apparent weight of the tellurium precipitated was in each case considerably greater than the calculated amount.

III. A determination of tellurium by means of sulphur dioxide and hydrazine hydrochloride was made in a weighed amount of pure tellurium dioxide. The tellurium thus obtained was again dissolved and the determination repeated. The results were as follows:—

Te found.—0·4045.	Te used.—0·4052.
„ 0·4034.	„ 0·4045.

IV. Exactly equivalent quantities of cadmium chloride and sodium tellurite, both in solution, were brought together, and the resulting precipitate filtered off. The clear filtrate was evaporated to a small bulk and treated with hydrogen sulphide. No precipitate was formed, showing that both cadmium and tellurium had been completely removed in the first precipitate. This precipitate, therefore, could have been nothing other than the normal tellurite.

Silver Tellurite.—When a solution of sodium tellurite is added to a solution of silver nitrate, a pale lemon-yellow flocculent precipitate is formed. This precipitate remains pale yellow as long as the silver nitrate is in excess, but when sodium tellurite is added in excess the colour of the precipitate quickly changes to white. On drying, both precipitates assume a buff colour, and are almost indistinguishable from each other. On standing, however, the one which was precipitated in presence of an excess of silver nitrate begins to turn dark in colour, and in the course of a week or two has changed completely to a dark bluish grey colour. The other does not change, and has actually been kept for twenty months without undergoing any modification.

Nevertheless, both of these precipitates have the same composition, and when dried both are anhydrous. In the following Table I. and II. were precipitated in presence of an excess of silver nitrate, while in III. and IV. the proportion was reversed.

Calculated for Ag_2TeO_3.—Ag, 55·14; Te, 32·59.
Found I.—Ag, 55·09; Te, 32·96.
Found II.—Ag, 54·90; Te, 32·51.
Found III.—Ag, 54·89; Te, 32·52.
Found IV.—Ag, 55·25; Te, 32·52.

Silver tellurite can exist in still other forms. When heated to a temperature of 250°, it becomes deep blue or purple in colour. This change takes place without any change in weight. On heating still higher, to 450° or 500°, it again changes to a pale yellow. In this last condition it can be cooled down to ordinary temperatures unchanged, providing it is not disturbed during the cooling. But if during this cooling, and while it is still quite hot, it is disturbed by compression with a glass rod, the mass immediately changes to the purple variety.

Again, when freshly precipitated silver tellurite is treated with ammonium hydroxide it dissolves immediately, and when the solution is allowed to evaporate spontaneously brownish yellow crystals deposit. These crystals contain neither ammonia nor water, and can be heated to 500° or higher without any change in weight. On cooling, after being thus heated, these crystals again yield the ordinary pale yellow silver tellurite.

It thus appears that silver tellurite can exist in a number of different varieties. The freshly precipitated salt is soluble in acetic and tartaric acids, also in nitric and sulphuric acids. Hydrochloric acid decomposes it with the formation of silver chloride and tellurium tetrachloride. It is insoluble in water.

An attempt was made to obtain silver tellurite in crystalline form in the same way in which Hutchins crystallised some of the precipitated tellurates (*Journ. Am. Chem. Soc.*, 1905, xxvii., 1157). The method was to allow the precipitate to stand in contact with water containing minute quantities of free acids. This method, however, proved unsuccessful with the tellurites. It might be stated that the precipitated tellurites as a rule show very little or no tendency to pass into the crystalline state.

Nickel Tellurite.—$NiTeO_3.2H_2O$ was obtained as a pale greenish yellow precipitate on adding a solution of sodium tellurite to a solution of nickel chloride. The precipitate was light and amorphous.

Calculated.—Ni, 21·72; Te, 47·21; H_2O, 13·32.
Found.—Ni, 21·40; Te, 47·96; H_2O, 13·62.

When heated, the light yellow-green tellurite loses water and turns to a light brown colour.

Cobalt Tellurite.—$CoTeO_3.H_2O$ was obtained by precipitation from a solution of cobalt chloride as a dark,

purple-blue insoluble substance. When heated to 300—400° it melts without change of colour, losing water at the same time.

Calculated.—Co, 23·36; Te, 50·52; H_2O, 7·12.
Found.—Co, 23·39; Te, 50·30; H_2O, 7·79.

Manganese tellurite is a very unstable compound. When a solution of manganous chloride is added to a solution of sodium tellurite, there forms a voluminous white precipitate, which is faintly pink or flesh-coloured. On standing, the colour gradually changes to a deep chocolate-brown. The change takes place more rapidly when it is brought into direct contact with air. This change is due to oxidation of the manganese to the trivalent state. When the chocolate coloured substance is treated with hydrochloric acid, a dark, greenish brown solution of manganic chloride is formed. This colour is discharged by diluting the solution with water, or by boiling; in the latter case chlorine is evolved.

If the precipitation is carried out with solutions which have been previously thoroughly boiled to expel the air, the precipitate is perfectly white, and remains so as long as contact with air is avoided.

The extent of oxidation was determined by boiling the material with hydrochloric acid, distilling the chlorine into a solution of potassium iodide, and titrating the iodine with sodium thiosulphate. The tellurium was precipitated from the hydrochloric acid solution by sulphur dioxide and hydrazine hydrochloride. Finally the manganese in the filtrate from the tellurium was precipitated as manganese ammonium phosphate, ignited to pyrophosphate, and weighed. The water was estimated by difference.

The atomic ratio of manganese to tellurium was found to be 1 : 1, so that the precipitate first formed was undoubtedly normal manganous tellurite. The ratio of active oxygen to manganese, however, was less than would be required for complete oxidation of the manganese to the trivalent condition, and this ratio also varied in different samples. One sample of the freshly prepared precipitate was washed by decantation, and suspended in water, while air was bubbled through the mixture for a week. Analysis showed that only about 28 per cent of the manganese was oxidised.

The freshly precipitated manganese tellurite seems to be more sensitive toward oxygen than after it has stood for some time. White manganese tellurite was prepared by bringing together under a layer of melted paraffin freshly boiled and air-free solutions of manganese chloride and sodium tellurite. The precipitate was allowed to stand unoxidised for a week, after which it was treated for two weeks with a current of air, as in the previous case. The colour changed to brown. A determination of the active oxygen indicated that about 20 per cent of the manganese had been oxidised.

Another sample of the precipitated manganese tellurite was dried, pulverised, and left in contact with air for three weeks. At the end of this time about 38 per cent of the manganese was oxidised, and the powder had the following composition :—$3Mn_2O_3.10MnO.16TeO_2.10H_2O$.

Calculated for $3Mn_2O_3.10MnO.16TeO_2.10H_2O$.—Mn, 22·46; Te, 52·11; Active O, 1·22; H_2O, 4·59.
Found. Mn, 22·26; Te, 52·39; Active O, 1·24; H_2O, 4·49.

It is probable that complete oxidation of the manganese would be accomplished in time.

Lead Tellurite.—This compound was prepared by precipitation from a solution of lead nitrate. It forms as a white flocculent precipitate.

Calculated for $3PbTeO_3.2H_2O$.—Pb, 52·45; Te, 32·35; H_2O, 3·04.
Found.—Pb, 52·09; Te, 32·26; H_2O, 3·20.

Oxidation of the Tellurites.—Shortly after the work on the tellurites was undertaken it was discovered that many of the tellurites oxidise when heated in the air under certain conditions. This fact seemed to have escaped the notice of Berzelius and other investigators, as no mention of it has been found in the literature. On account of this oxidation it is not possible to prepare the tellurites, free from tellurates, by the fusion of tellurium dioxide with carbonates, as suggested by Berzelius, without first excluding air from the mixture. Hence, in the preparation of the alkaline tellurites, the fusion was carried out in an atmosphere of carbon dioxide, as already mentioned. Tellurites which are thus prepared are completely free from tellurates, but when the precaution to exclude air during the fusion is neglected, the product always is contaminated to a greater or less extent with tellurate.

In order to ascertain how far it is possible to oxidise the tellurites by heating in the air, the following experiment was carried out. Some potassium tellurite was finely pulverised, and then spread out in a thin layer on the bottom of a crucible. The crucible was partly immersed in a bath of melted lead whose temperature was kept at 460—470°. At intervals, portions of the material were removed for analysis. The proportion of tellurate was determined by boiling the mixture with hydrochloric acid, distilling the chlorine into a solution of potassium iodide, and titrating the iodine with sodium thiosulphate. The results are given in the following table, which gives the time of heating together with the corresponding amount of potassium tellurate.

Time (in hours).	K_2TeO_4 (per cent).
10	26·88
20	52·88
30	80·99
38	94·49
43	97·86
57	99·47

The final product was next analysed with the following results :—

	Found.	K_2TeO_4.
K	29·11	29·01
Te	47·02	47·28

In this connection it is interesting to note that when potassium tellurate is heated to redness, it loses oxygen and is reduced to tellurite. Thus between 450° and red heat we have a reversal of the reaction.

$$2K_2TeO_3 + O_2 \rightleftarrows 2K_2TeO_4.$$

Normal sodium tellurite behaves in a manner exactly similar to the potassium tellurite.

Time of heating (in hours).	Na_2TeO_4 (per cent).
10	35·09
20	64·77
30	90·76
40	99·09
50	99·49

While the normal alkaline tellurites can be oxidised quite readily, the ditellurites behave somewhat differently. Potassium ditellurite can be oxidised, but the reaction proceeds much more slowly than in the case of the normal salt. Furthermore, only one-half of the tellurium seems to be oxidisable to the higher state of oxidation. The experiment was carried out in the same way as with the normal tellurites except that the temperature was kept at 440—450°, on account of the lower melting-point of the ditellurite. The results obtained were as follows :—

Time of heating (in hours).	Active O (per cent).
19	1·18
46	2·00
89	2·81
156	3·28
221	3·54

The content of active oxygen required by the formula $K_2OTeO_3.TeO_2$ is 3·72 per cent, and that for complete conversion to ditellurate would be 7·18 per cent. It will be seen that the content of active oxygen seems to approach the former figure as a limit.

The ditellurite of potassium is white, but when it is oxidised as above, it is slightly brown in colour. This brown product belongs to a class of compounds which are formed as intermediate products in the oxidation of tellurium dioxide to trioxide, by means of alkaline oxidising agents. These compounds Berzelius thought to be tetra-tellurates, but they have been shown by the work of Lenher and Potter (*Journ. Am. Chem. Soc.*, 1909, xxxi., 24) to have a more complex as well as variable composition. Their composition might be represented by the general formula $m(K_2O).n(TeO_3).p(TeO_2)$, in which m, n, and p may be all different or all alike. These substances have been obtained by fusing tellurium dioxide with potassium nitrate or chlorate, and also synthetically by heating the dioxide with potassium tellurate. In the oxidation of the ditellurite of potassium to $K_2OTeO_3.TeO_2$, as described above, we are approaching the same class of compound from another direction. In this case, however, the composition is simpler and more definite.

Sodium ditellurite was also heated in the same way as the corresponding potassium salt, but after five days of heating it showed only a slight trace of oxidation. Neither the tetratellurites nor pure tellurium dioxide show any oxidation under similar treatment. It is therefore evident that with a higher content of tellurium dioxide the power of the tellurites to take up oxygen from the air decreases.

The normal tellurites of most of the other metals, with the exception of silver, can also be oxidised, but the rate of oxidation is very much lower than in the case of the normal tellurites of the alkali metals.

It has been stated, in describing the methods of analysis, that water was usually determined by loss of weight on heating. In view of the fact that the tellurites take up oxygen on heating, it would seem that this method of determining water would give low results. But, excepting the normal alkaline tellurites, the oxidation is so slow that the error arising from this source would be imperceptible. Thus when anhydrous magnesium tellurite is heated to 450° for 15 hours, the gain in weight due to oxidation is only 0·25 per cent, and in 77 hours it is only 1·5 per cent. Again, nickel tellurite after being heated at 450° for 70 hours, contained only 0·46 per cent of active oxygen. In contrast with these long periods of heating, the length of time necessary to drive off all the water is only 15 minutes.

Summary.

1. The tellurites of the alkaline metals can be prepared by fusing together tellurium dioxide and a metallic oxide, hydroxide, or carbonate. Since, however, tellurous acid forms salts of different types, namely, the mono-, di-, and tetratellurites, the starting material must be used in definite proportions in order to obtain a tellurite of definite composition. The tellurites of the heavier metals are best prepared by double decomposition.

2. The alkaline tellurites are soluble, the alkaline earth tellurites are slightly soluble, and those of the heavy metals are insoluble.

3. As a class, the tellurites are unstable compounds. Tellurous acid is easily displaced at ordinary temperatures in presence of moisture by carbon dioxide.

4. The tellurites can be oxidised by heating in the air at a temperature of 440—470°. This oxidation is fairly rapid in the case of the normal alkaline tellurites.

5. The tellurites of most of the metals other than potassium and sodium, as well as the ditellurites of the alkali metals, oxidise when heated much more slowly than the normal alkaline tellurites.

6. In potassium ditellurite, only one-half of the tellurous acid is oxidisable by this means, forming the compound $K_2O.TeO_3.TeO_2$. The tetratellurites are not oxidisable by heating in the air at 450°, neither is pure tellurium dioxide.

7. Manganous tellurite will oxidise on contact with the air at the ordinary temperature, but in this case the manganese is oxidised, passing to the trivalent state.

8. Ammonium tellurite probably exists in solution, and also in the solid state when surrounded by a saturated solution of tellurous acid in ammonia, but otherwise decomposes spontaneously at the ordinary temperature, forming hydrated tellurium dioxide.

9. Silver tellurite can be obtained in a number of different varieties. When precipitated in presence of an excess of sodium tellurite, it is white, but when silver nitrate is in excess, the precipitate is of a pale yellow colour. This second form in the course of a few days turns to a bluish grey powder, while the first is stable. At 250° both turn to a deep purplish blue colour. Still, another variety can be obtained, by crystallising from an ammoniacal solution, as a deep brownish yellow substance. All of these forms are anhydrous.

10. The precipitated tellurites are all flocculent and amorphous, and with the exception of the magnesium salt, show practically no tendency to become crystalline.

11. These precipitates are very apt to occlude other salts as impurities, which are very difficult to remove. This tendency is most marked in the barium salt, which will occlude large quantities of barium chloride. In the case of lead tellurite, which was precipitated from a solution of lead nitrate, the precipitate contained nitrates, but these were not so difficult to remove as the chlorides.

12. With the exception of the silver salt, these precipitates are all definite hydrates, which do not readily give up their water.

THE PHYSIOLOGICAL PRINCIPLES OF HEATING AND VENTILATING.*

By Professor LEONARD HILL, M.D., F.R.S.

LECTURE I.—THE QUALITIES OF EXPIRED AIR IN CROWDED AND CONFINED PLACES.

PROFESSOR LEONARD HILL began his lecture with a consideration of the atmosphere and its climatic variations, and the influence of the pressure of oxygen on life. In describing the mountain sickness which affects mountaineers and aeroplanists, when rapidly rising into the attenuated air of high altitudes where the pressure of oxygen has fallen from 21 per cent to 12 per cent of an atmosphere, he stated that the sickness is made worse by muscular effort, but instantly relieved by breathing oxygen, and he demonstrated the working of a very light portable apparatus for generating and inhaling oxygen. This apparatus is not, however, required by persons who live on heights, as the body quickly compensates for the lessened pressure of oxygen by concentration of the blood, and slowly by the formation of new red blood corpuscles. Those who dwell at high altitudes have less water and more red corpuscles and haemaphæbin in their blood. The lecturer also described the dangers to divers and caisson workers of breathing compressed air, which causes a solution of nitrogen gas in the watery fluids and the fat of the body. This gas may bubble off in the blood and disturb the circulation after the men have come out of the compressed air; but the danger can be prevented by proper methods of regulating the duration of work and the time of compression.

Passing to a consideration of the atmosphere of strictly confined places—sewers, wells, mines—the lecturer explained how de-oxygenated air collects, owing to the oxygen in the air being used up by the soil, and he demonstrated a second breathing apparatus by which rescue-work in de-oxygenated and irrespirable air is made pos-

* Chadwick Public Lectures, Bristol, 1913. (Delivered at Bristol University, October 23. The Vice-Chancellor, Sir Isambard Owen, M.A., M.D., in the Chair).

sible. Explosions in coal mines, so Professor Hill stated, could be prevented, if the oxygen in the air were lowered from 21 to 17 per cent of an atmosphere, and this would have no deleterious effect on the miners. The great explosions of recent years are due to the improved ventilation of mines.

The injurious effects of dust in the atmosphere were next dwelt upon. Lead-poisoning is due to inhalation of lead dust. Workers in silicated stones or metal suffer greatly from phthisis; and for these also there was shown an apparatus—simple in the working—by which fresh air can be blown over the mouths of workers in dusty trades.

Referring to the dust of the roads, the lecturer said every effort should be made to reduce it. Streets should be cleaned with water and not swept. Infection was certainly spread by dust, as also by insects and by the spraying of saliva in spitting, coughing, sneezing, and talking. Saliva spray is probably the chief cause of infection by common colds and phthisis. It is one which can be limited by training people to sneeze and cough into handerchiefs, and to speak, when infected with catarrh, into newspapers held in front of their faces.

Continuing the main discussion of his lecture, which was specifically on the qualities of expired air, Professor Leonard Hill said :—"It has generally been supposed that all the bad effects of close crowded places are due to chemical impurity of the air, that the air is contaminated by the exhalations of human beings, and that it becomes impoverished of oxygen. But what people always complain of is the heat and want of movement of the air." Proof lies that the excess of carbonic acid in the air in a crowded room if sufficient to have any effect at all will only make people breathe a little more deeply and ventilate their lungs more fully.

The oxygen in a crowded room is never diminished by more than 1 per cent, the cracks, crannies, and pores in the room always suffice to let fresh air in, so that the oxygen does not suffer a greater diminution. This diminution of oxygen has no physiological effect whatever. In the famous Alpine health resorts there is a greater diminution in the concentration of oxygen owing to the attenuation of the air at higher altitudes. Therefore the chemical state of the air, so far as regards carbonic acid and oxygen, has nothing whatever to do with the discomfort which is felt in crowded and confined places, or with the healthful effect of open-air life.

A great deal has been made of the supposed existence of volatile organic poison in expired air. Its existence is asserted in all the popular books of hygiene. There is no evidence, worth anything, in favour of the existence of this organic poison in expired air.

The unpleasant smell of crowded confined atmospheres are not smelt by the crowd within, but only by those who come in from the fresh air. There is no evidence that such smell has a poisonous effect, but it may nervously affect sensitive people, especially those who imagine it betokens the existence of a poison in the air; the smell may be prevented by cleanliness of person, clothes, and habitations.

Conclusive evidence will be brought forward in the next lecture to show that the physical conditions of the atmosphere, heat humidity and movement, very greatly influence our comfort and health.

Binary System of Thallous Chloride with Chlorides of Divalent Metals.—C. Sandonnini.—Unlike potassium chloride, which it resembles in some respects, thallous chloride gives with lead and stannous chlorides at high temperatures solid solutions in all proportions. With mercury chloride two compounds are formed, $TlCl.HgCl_2$ and $4TlCl.HgCl_2$ (?), the second of which was not known previously. With cadmium chloride thallous chloride gives only one compound, $TlCl.CdCl_2$, while with potassium chloride at a high temperature, in addition to the analogous compound, the compound $4KCl.CdCl_2$ is obtained.—*Atti Reale Accad. dei Lincei*, xxii., [ii.], No. 1.

THE SCIENTIFIC WEEK.

(From Our Own Paris Correspondent).

INTERNATIONAL CONFERENCE ON THE METRE.

The International Conference on the Metre has just opened at the Ministry of Commerce, under the presidency of Prof. Appell, Member of the Academy of Sciences. It has come to several important decisions; first of all, the delegates have verified the standard kilogrms. of the different countries adhering to the convention of the metre. Only the Danish, Hungarian, and Servian kilogrms. have undergone important alterations. The kilogrms. of the other nations had not varied a hundred millionth of their weight, which would be a small error, equal to that which would be made if one made the mistake of the earth's meridian. The Conference has also decided that the States that possess geodesic bases shall exchange amongst themselves the Invar wires, so as to verify, very precisely, the length of these bases. Moreover, the standards with ends that are used to give the calibre to pieces of machinery will have a definition temperature equal to zero degrees. Thus in the whole world there will be one single scale for the construction of machinery. The Conference has foreseen the time when the temperature scales actually in use will be abandoned. The hydrogen thermometers are those by which low temperatures may be attained; temperatures of $-252°$ to $-271°$, which is the temperature of the liquefaction of helium. Preparatory studies are soon to be undertaken in order to reach, in a near future, a scale of a still greater elasticity, that of thermodynamic temperatures.

PREHISTORIC ART.

In a Grotto situated near Poncin, at the spot called La Colombière (Ein), two *savants*, MM. L. Mayet and J. Pissot, have just discovered a bone of a mammoth engraved with a human face. When presenting their notice to the Academy, M. Donvilli indicated that this engraved bone was found in the upper auragnacian stratum. Our prehistoric ancestors have traced on this mammoth bone the profile of a man with a convex forehead, a very high fac[illegible] lengthened by a beard, indica[illegible]d by batchings beneath [illegible] chin. The nose is long and [illegible], the pilosity of the tr[illegible] is abundant. Above it is to be seen a female outline, representing only the middle part of the body.

THE TOTAL CUBE OF THE [illegible]ATER OF THE EARTH.

Professor W. Halbf[illegible] reckons that the total cube of water of the terrestrial globe is 1,304,068,550 cubic kilometres. The greater part of this volume, that is to say 1,300,000,000 cubic kilometres, is in the Oceans. Next in order of importance comes the quantity of water contained in the icy regions, especially the ice of the Poles, that is to say 3—5 millions of cubic kilometres. The lakes and ponds would contain 250,000 cubic kilometres, the subterranean waters a similar quantity, the rivers 50,000 cubic kilometres, atmospheric water 12,300, the marshes 6000, and the snow on the surface of the ground 250,000 cubic kilometres. The total volume of the terrestrial globe being 1,083,205 millions of cubic kilometres, the volume of the waters is equal to 1/830 of the volume of the Earth.

A CURE FOR THE SLEEPING SICKNESS.

The researches of learned men concerning one of the most terrible diseases of the Black Continent, the sleeping sickness, have very much increased during the last few years, without, however, any definite result having been obtained. In a paper recently presented before the Academy of Sciences by M. Laveran, M. Danyez, of the Pasteur Institute, signals the fact that, in the treatment of trypanosomiasis, it is advantageous to make use of several medications, not one alone being sufficiently energetic to cure the disease. Thus, the simultaneous employment of several arsenical combinations, such as arsenious acid, orpiment, and atoxyle, gives very interesting results. M.

Danyez has tried to obtain a solution of arseno-benzol and nitrate of silver. This combination has had a very energetic action on animals attacked by trypanosomiasis. In *surra* and in trypanosomiasis occasioned by the spirilla of Rhodesia—the same microbe as that of the sleeping sickness—exceedingly remarkable results have been obtained with very small doses of arseno-benzol and nitrate of silver. A single injection of one-twentieth part of a milligrm. has sufficed to cure a mouse weighing 20 grms., and rabbits weighing 2 or 3 kilogrms. were cured by a single intra-venous muscular injection of 5 milligrms. of this new product.

NOTICES OF BOOKS.

Organic Chemistry for Advanced Students. Volume II. By Julius B. Cohen, Ph.D., B.Sc., F.R.S. London: Edward Arnold. 1913.

This is a valuable text-book of organic chemistry for advanced students, and if the author's suggestions as to the order in which the chapters are read are followed a good grasp of the fundamental principles and of the recent development of the subject should be acquired. A description of the details of the individual substances of organic chemistry is not given, but rather a general survey of the nature and dynamics of organic reactions, and such difficult subjects as the connection between molecular structure and the more important physical properties are excellently treated. Modern theories of the causes of colour and its connection with structure are discussed in a particularly interesting and up-to-date chapter. The book has an exceptionally high educational value, and it strikingly exemplifies the recent changes and improvements which methods of teaching organic chemistry have undergone.

A Systematic Course of Practical Science for Secondary and other Schools. Book II. *Experimental Heat.* By Arthur W. Mason, B.Sc., B.A. (Lond.). London: Rivingtons. 1913.

This book describes an excellent course of experimental work in Heat, and in all respects it is quite up to the high level of the first volume on Introductory Physical Measurements. Every effort is made to encourage the student's independence and self-reliance, and if he works carefully through the course he can hardly fail to become an accurate and exact worker. The book is intended for rather older pupils than the introductory course, and those who use it are supposed to have some knowledge of the best methods of recording results and describing experiments. The apparatus required is in all cases quite simple, and the directions are very detailed and precise. Additional questions involving calculations are given in great abundance, and also some extra practical exercises. The importance of the use of graphical methods of representing results is emphasised, and by his questions and hints the author shows that he thoroughly understands the usual difficulties of the beginner, and knows exactly how to help him to find his own way out of them.

Brazil in 1912. By J. C. Oakenfull. London: Robert Atkinson, Ltd. 1913.

A glowing account of the resources and possibilities of Brazil is to be found in the fourth annual edition of this handbook. Intending settlers can derive from it much information about the laws, the state of education, the cost of living, salaries, &c., and the various industries, and the illustrations are a very attractive feature. The author is an enthusiastic believer in the successful future before Brazil, and his comments and advice to colonists appear to be apposite and worthy of careful attention.

On the Circulation of Energy and Matter. By Edward M. Darken. Wellington, New Zealand. 1913.

The author of this pamphlet believes that he has discovered the key to the solution of the problem of the origin of life, and he has worked out a theory of the formation of the living cell from a droplet of water by the force of suction. Matter itself he would regard as being made by the sun, which is "alive just as much as we are." He states his argument in a very condensed form, and makes many assertions which are at variance with commonly accepted opinions without bringing forward any proof of them. However, his speculations and reflections may possibly interest the somewhat limited public to whom they are addressed.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Academie des Sciences. Vol. clvii., No. 7, August 18, 1913.

Absorption Bands in Ultra-violet Spectrum of Alcohols of the Fatty Acids.—MM. Massol and Faucon.—The spectra of the two abnormal primary alcohols, 2-methyl-3-propanol-2-methyl-1-butanol and 2-methyl-4-butanol, show two absorption bands between λ 2500 and λ 2700, and λ 3060 and λ 3150. These two absorption bands are peculiar to these alcohols, and are not found in the fundamental hydrocarbon, nor in the other alcohols or their halogen derivatives. The aldehydes give a single broad band corresponding approximately to radiations intermediate between those of the two bands of the alcohol.

No. 8, August 25, 1913.

Isomerisation of $\beta\gamma$-Unsaturated-α-hydroxyl Acids to form γ-Ketone Acids.—J. Bougault.—By the action of acids of medium strength (oxalic or phosphoric) α-phenyl-oxycrotonic acid is partially transformed into γ-phenyl-oxycrotonic acid. Thus in all probability the transformation of the $\beta\gamma$-unsaturated α-hydroxyl acids into γ-ketone acids begins with the formation of $\alpha\beta$-unsaturated γ-hydroxyl acids and no other intermediate term is formed. The following formulæ show the changes that occur:—

$$R.CH.=CH.CHOH.CO_2H \rightarrow$$
$$R.CHOH.CH=CH.CO_2H \rightarrow R.CO.CH_2.CH_2CO_2H.$$

Bulletin de la Société Chimique de France. Vol. xiii.-xiv., No. 15, 1913.

Relations of Isomorphism in the Organo-metallic Series.—Paul Pascal.—The thermic analysis of binary mixtures of the monohalogen derivatives of benzene shows that the four halogens can be divided into two groups. The first group consists of fluorine alone, which is different from any of the others, since benzyl fluoride always gives a eutectic when it is mixed with the homologous halogen derivatives. The other group contains chlorine, bromine, and iodine, which taken in pairs always give a continuous series of mixed crystals. Chlorine and bromine resemble one another more than they resemble iodine. These results agree with those obtained when the halogens are regarded from a chemical point of view. If mixtures of benzyl cyanide with the benzyl halogen derivatives are analysed by the thermic method it is found that the cyanogen group does not resemble the chlorine-bromine-iodine group.

Atti della Reale Accademia dei Lincei. Vol. xxii. [i.], No. 12, 1913.

Ortho-halogen Derivatives of Paranitroaniline.—G. Körner.—If paranitroaniline is dissolved in hydrochloric acid and chlorine or bromine is passed into the

solution, a mono or dihalogen derivative is readily obtained. Thus, if chlorine is introduced into the boiling solution in the proportion of one molecule to one molecule of the aniline derivative, orthochloro paranitroaniline is obtained, while at the ordinary temperature the dichloro-derivative is formed. The bromine compounds can be prepared similarly, and the iodine compounds by using iodine chloride. In the last case a mixture of the mono- and di-derivative is obtained, and may be separated into its constituents by treating with alcohol, in which their solubilities are very different.

Polyazoxy Compounds.—A. Angeli.—Bisazoxybenzene (melting-point, 155°) when treated with concentrated sulphuric acid at 100° gives two products, the formula of the first of which is undoubtedly $C_6H_5.N_2.C_6H_4.N_2.C_6H_4(OH)$. It furnishes an ethyl ether which fuses at 138°. When sulphuric acid acts on bisazoxybenzene at 0° two yellow products, both insoluble in alkalis, are formed, and a third, red product which is easily soluble in soda. The first of these is an isomer of the original substance, fusing at 168°. It is reduced by means of aluminium amalgam to Mills's bisazobenzene. The soluble product fuses at 148°, and appears to be a third isomer. These three isomers can probably be represented by the formulæ:—
α-Form,—

$$C_6H_5.\underset{\underset{O}{\|}}{N}{=}N.C_6H_4.N{=}\underset{\underset{O}{\|}}{N}.C_6H_5$$

melting-point, 168°. β-Form,—

$$C_6H_5.N{=}\underset{\underset{O}{\|}}{N}.C_6H_4.\underset{\underset{O}{\|}}{N}{=}N.C_6H_5$$

melting-point, 155°. γ-Form,—

$$C_6H_5.\underset{\underset{O}{\|}}{N}{=}N.C_6H_4.\underset{\underset{O}{\|}}{N}{=}N.C_6H_5$$

melting-point, 148°.

Compounds of Ferric Urea.—A. Barbieri.—When a solution of ferric perchlorate, acidified with perchloric acid, is added to a concentrated solution of urea, crystals of perchlorate of ferric urea, $\{Fe(CON_2H_4)_6\}(ClO_4)_3$, exactly analogous to the similar chromium salt, separate out. Other salts of ferric urea can be obtained, *e.g.*, the nitrate (from ferric nitrate and urea), the permanganate (from the nitrate and sodium permanganate), the bichromate, the chloride, bromide, and nitratoperiodide. The complex $[Fe(CON_2H_4)_6]$ is less stable than $[Cr(CON_2H_4)_6]$. The dilute solutions of salts of ferric urea are yellow, and give ferric hydrate with ammonia in the cold.

Vol. xxii., [ii.], No. 1.

New Derivatives of Artemisine.—E. Rimini and T. Iona.—An α-tetrahydroartemisine can be obtained by passing a current of hydrogen through an alcoholic solution of artemisine in presence of colloidal palladium. The substance may be re-crystallised from benzene, and from the mother-liquor a second derivative, β-tetrahydroartemisine, may be separated by fractional crystallisation. Both compounds readily yield semicarbazones and oximes, and the acids may be obtained by dissolving the artemisine in N/10 caustic soda solution, adding a small excess of N/10 sulphuric acid, cooling, extracting with chloroform, and evaporating off the solvent.

MISCELLANEOUS.

Mining Exhibition, South Africa.—*Preliminary Announcement.*—The Third Annual Mining Exhibition, under the auspices of the Chemical, Metallurgical, and Mining Society of South Africa, will be held in Johannesburg during the month of April, 1914, when it will remain open for about two weeks. The scope of the Exhibition will be on much the same lines as in previous years, *i.e.*, Chemical, Metallurgical, and Mining apparatus and devices for laboratories, works, and mines; models, working or otherwise, of apparatus for similar purposes; plans, diagrams, &c., of mines, works, plants, machinery, and apparatus; safety and rescue, and other ambulance apparatus and appliances; and specimens of crude and manufactured mineral or other natural products of South Africa. The Exhibition is primarily for the benefit and information of those engaged and interested in mining work, and to give those in search of mineral products an opportunity of ascertaining where these products may be obtained. The two previous Exhibitions have been visited by something like 30,000 persons, admission has been free, and no financial gain has accrued to the Society, which has organised the Exhibition solely for the purpose of bringing to the notice of those engaged in the mining industry the latest developments in everything likely to be used on or in the mines of South Africa.

MEETINGS FOR THE WEEK.

Monday, Nov. 3rd.—Royal Institution, 5. General Meeting.
—— Society of Chemical Industry, 8. "Studies in Oxidation—IV., The Production of Oxygen by Electrolysis—Peroxidation as Determined by Platinum and other Catalysts," by H. E. Armstrong. "Analysis of Crude Glycerin by the International Standards Methods, 1911—Determination of Organic Residue," by R. G. Grimwood. "Observations on the Abel Heat Test," by B. J. Smart.

Wednesday, 5th.—Society of Public Analysts, 8. "Preparation of Rubber for Analysis," by L. Archbutt. "The Examination of Commercial Gelatines in reference to their Suitability for Paper-making," by R. W. Sindall and W. Bacon. "Experiments on Chlorine Compounds of Ethane and Ethylene, with special reference to their application to Analytical Chemistry," by L. Gowing-Scopes. "Detection and Estimation of B[illegible]oic Acid in Milk and Cream," by E. Hinks.

Thursday, 6th.—Chadwick Public Lectures, 5. (The University, Bristol). "Physiological Principles of Heating and Ventilating," by Dr. Leonard Hill.
—— Royal Society. "The Soil Solution and the Mineral Constituents of the Soil," by A. D. Hall, W. E. Brenchley, and L. M. Underwood. "Studies in Heredity—II., Further Experiments in crossing British Species of Sea Urchins," by E. W. MacBride. "Synthesis by Sunlight in Relationship to the Origin of Life—Synthesis of Formaldehyde from Carbon Dioxide and Water by Inorganic Colloids acting as Transformers of Light Energy," by B. Moore and T. A. Webster. "The Trypanosomes causing Dourine (Mal de Coït or Beschälseuche)," by B. Blacklock and W. Yorke. "Postural and Non-postural Activities of the Mid Brain," by T. G. Brown. "Nature of the Coagulant of the Venom of *Echis carinatus*," by J. O. W. Barratt.
—— Chemical Society, 8.30. "Conversion of Orthonitroamines into Oxadiazoleoxides (Furazane-oxides)," by A. G. Green and F. M. Rowe. "Constitution of Aniline Black," by A. G. Green and W. Johnson. "Constituents of Senna Leaves," by F. Tutin. "Study of some Organic Derivatives of Tin as regards their Relation to the Corresponding Silicon Compounds—Part II., Condensation Products of Dihydroxydibenzylstannane," by T. A. Smith and F. S. Kipping. "Series of Mixtures of Nitro-compounds and Amines, which are Coloured in the Liquid State only," by C. K. Tinkler. "6'-Aminoquercetin," by E. R. Watson. "Measurement of the Rate of Reaction by the Change of Volume in Solution," by R. Wright. Amalgams containing Silver and Tin," by W. A. Knight and R. A. Joyner. "Action of Chlorine on *m*-Iodoaniline and on *m*-Bromoaniline," by H. McCombie and P. J. Ward. "Guanidinium Nitrite and its Decomposition under Heat," by P. C. Ray, M. L. Dey, and S. C. Jana. "Absorption of Light by Uranous Chloride in different Solvents," by T. R. Merton. "Influence of Solvents on the Rotation of Optically Active Compounds—Part XIX., The Rotation of certain Derivatives of Lactic Acid," by T. S. Patterson and W. C. Forsyth. "Action of Nitrogen Iodide upon Methyl Ketones," by F. D. Chattaway and R. R. Baxter.

THE CHEMICAL NEWS.

VOL. CVIII., No. 2815.

DETERMINATION OF MELTING-POINT BY THERMOMETER BULB METHOD.

By ROBERT MELDRUM.

THIS method of determining the melting-point of waxes, fatty acids, fats, and organic compounds in general is used extensively in analytical work, but frequently the results obtained have shown a wide variation in the melting-point in the same sample. This has given birth to the general opinion amongst analysts when dealing with solid fats and waxes that the melting-point is affected according to the prolonged melting and rapid cooling of the fat. After the thermometer has been coated with the substance it is generally assumed that a long interval of time must elapse, two, six, twelve, and even twenty-four hours, before the fat attains its normal condition. The accepted theory is that the fat, after being melted and solidified rapidly, has undergone molecular or physical changes which increase or decrease the melting-point beyond the normal. That this theory persists extensively is shown by a great deal of the literature dealing with the melting-point and solidifying-point of fatty substances, where nearly, without exception, great reliance is placed in melting the fat a few degrees above its melting-point, and not for too long. The temperature at which the substance is melted, the time during which it remains melted, and the cooling down process have all become to be considered as important points connected with regularity in melting-point and solidifying-point determinations. Very little work has been done in the investigation of the rising and falling of the melting-point above normal, due to thermal and other physical conditions inherent in the heating and cooling. That the solidifying-point may go considerably beyond the normal when ultra conditions are present is seen in Deprez's experiment of cooling down water to −20° C. without solidifying. But so far as the author's experience goes, extending over the past twenty years, and dealing with all classes of fatty matter, the variation in the thermometer bulb method of determining the melting-point is not due to the thermal treatment of the fat but to errors in manipulation. The following fats were melted and thermometer dippings made and placed aside for various intervals of time, and the melting-point taken, the same thermometer being used throughout:—

Mutton Tallow and Fatty Acids (0° C.).

	10 mins.	15 mins.	30 mins.	2 hrs.	16 hrs.
Mutton tallow	48·4 48·0 48·4		48·4	48·0	48·5
Fatty acids		47·6	47·6		47·8
	50·6 50·6 50·4				50·4
	38·8 38·8 39·0				39·0 39·2

The thermometers used for this method by various observers differ greatly in the size of bulb, and this has an important influence on the melting-point. When the bulb is small it is more sensitive to heat, in so far as it indicates changes in T° rapidly, whereas with the large bulb the changes are slower. With the large bulb the heating must be slower; if too rapid the readings will be low. But this question of large and small bulb is easily decided in favour of the former, as then the coating of fat is directly on the bulb or at the point where the temperature is indicated. It is needless to say that in all melting-point determinations good thermometers must be used divided into one-tenth degree.

The most convenient apparatus for determining the melting-point by this method is a tall beaker, about 7 in. long by 3 in. diameter, to which is fitted a bung. A test-tube 7 in. by 1 in. is passed through the bung in the centre. A glass stirrer in the form of a plunger to work up and down the *outside* of tube is also fitted. The beaker is filled with water. The thermometer with its layer of melted fat is fixed centrally in the test-tube by means of a bung. During the heating the water must be kept in complete circulation.

The sample of fat, if containing moisture or suspended matter, must be filtered through hot water funnel containing several layers of filter-paper. The fat is melted at 10° above its melting-point, but the author has never found the melting-point of any fat to be altered when maintained at even 212° F. for eight hours, nor by repeated re-melting and solidifying. This is the last cause to be looked for in explanation of any variation in the melting-point.

The most important point connected with the manipulation is coating the bulb with the fat. When the melting-point of fat is high, if the thermometer is rapidly dipped in and out, the coating of fat will be thick, and when the melting-point is determined an opaque drop is likely to be formed with low results. If the cold thermometer is dipped into fat and allowed to remain for a few seconds and then withdrawn, the film of fat will be thin, only sufficient fat being on bulb to form a drop slowly and above the normal melting-point. On the other hand, with low melting mixtures, even with the thermometer cold and rapidly dipped in and out of fat, the coating is often too thin, and gives high readings. With these very soft mixtures it is essential to cool the bulb down to 0° or −5° C. with ether or carbon bisulphide, and then to make a rapid dip. Some variation in the manipulation is required when dealing with some waxes and solid glycerides to obtain coatings of proper thickness. To ascertain when the coating is of proper thickness the author has been accustomed to melt the sample about 10° above its melting-point, and to make a rapid dip in and out, and cool for fifteen minutes, at 10° at least below its melting-point. When the melting-point is determined and if the first drop of fat that appears is opaque, the coating is too thick, and if the drop of fat hangs too long on the bulb, and if a second drop fails to appear, the coating is too thin. The thermometer is now cooled or heated 5° or 10°, as the case may be, and a rapid dip in and out made, and the melting-point again determined. Previous to determining melting-point the fat on apex of bulb ought to be removed by piece of filter-paper, otherwise the readings will be too high. Failure to remove the fat from apex will often result in erratic readings. In this way the T° to which the thermometer must either be heated or cooled is readily ascertained. Sufficient fat ought to be on the bulb to form two drops, as will be seen from the following examples:—

Mutton Tallow (0° C.).

First drop appears ..	48·4	48·0	48·4	48·0	48·5
First drop off	48·6	48·2	48·6	48·2	48·7
Second drop appears	48·7	48·4	48·8	48·3	48·9
Second drop off ..	48·8	48·6	49·0	48·6	49·1

Mutton Tallow Fatty Acids (0° C.).

First drop appears ..	47·6	47·8	47·8
First drop off	48·0	48·0	48·0
Second drop appears	48·2	48·2	48·1
Second drop off ..	48·4	48·5	48·2

The thickness of coating is of first importance. The thick coating acts as a heat insulator to the bulb, and requires extra slow heating to allow bulb to attain actual temperature of the fat. Moreover, due to these thick films, the flow to form a drop is quicker, forming globules of opaque and semi-melted fat. These opaque drops are really mixtures of solid and liquid fat, the viscosity of the mixture being higher than the liquid fat itself. The movement of these opaque drops depends on the mass of fat itself. When the viscosity of the molten fat is high, time is required to form a drop; if the heating is too rapid a T°

above the actual melting-point is required to produce sufficient viscosity to flow.

This question of viscosity plays a very important part in all methods used for determining the melting-point. At the critical point, when a solid is changing into the liquid state, very high viscosity at this point results, which frequently cause enormous pear shaped drops to form, and which tenaciously hang to the bulb and then drop off as a semi-solid. Due to this cause some waxes and fats will form drops which fall as threads. With some mixtures the whole of the fat on the bulb will slip off before the actual melting-point is attained. It would therefore appear on these theoretical grounds that the melting-point by this method is too high, due entirely to the phenomena of viscosity and also to the change in density which takes place at the critical point. As is well known, the glycerides have a higher viscosity at all temperatures than their fatty acids, but with the solid glycerides, and no doubt wax alcohols, the viscosity at the critical point when the solids change into liquids must be so great that no flow will take place at the melting-point, but only at temperatures above same.

From these considerations it will be evident that as the melting-point is approached the speed of heating must be very slow to allow sufficient time for the drop to form. Two minutes per °C. is not too slow. Within 2° of the melting-point the author is accustomed to remove the source of heat for two to three minutes until the thermometer ceases to rise, and then apply the heat again, and when 0·5° C. from the melting-point, again removing the flame, and maintaining it at this for two to three minutes, and so on till the drop forms.

Forty-five determinations of various mixtures of stearic and oleic acid with melting-point varying from 32·8 to 55·8, the maximum variation was 0·6° C.

The following fifty-nine determinations as detailed below also show the maximum variation not to exceed 0·6° C.:—

Melting-point by Thermometer Bulb Method.

Materials.	Melting-point °C.	Diff.
Stearine	56·0 56·0	—
80 per cent stearine, 20 per cent mineral oil ..	53·0 52·8	0·2
60 per cent stearine, 40 per cent mineral oil ..	51·0 51·2	0·2
40 per cent stearine, 60 per cent mineral oil ..	45·8 46·1	0·3
20 per cent stearine, 80 per cent mineral oil ..	39·8 40·4	0·6
Mutton tallow	48·3 48·2 48·4 48·4	0·2
Mutton tallow acids ..	46·8 46·8 47·0	0·2
Mutton tallow	48·4 48·0 48·4 48·0 48·5	0·5
Mutton tallow acids ..	47·6 47·8 47 8	0·2
Mutton tallow	50·0 50·0 50·6 50·3	0·6
Mutton tallow acids ..	49 8 50·0 50·0 49·8	0·2
Beef tallow	46·6 46·3	0·3
Beef tallow acids	43·8 44·0 43·6	0·4
90 mutton tallow, 10 hard oil	48·0 47·6 47·8 48 3	0·5
80 mutton tallow, 20 hard oil	47·4 47·2 47·6 47·4	0·4
Stearine	55·8 55·4 55·6 55·6 55·4	0·4
20 stearine, 80 oleic acid	32·8 33·0 33·2 33·4 33·2	0·6
Spermaceti	45·3 45·3 45·4	0·1

Time has not been available to investigate other methods of determining the melting-point, and how far these compare in accuracy with the thermometer bulb method. Nor has the author determined how far the results obtained by this method agree with the actual melting-point. This would require an enormous amount of labour. With stearic acid the melting-point is about 0·8° C. higher than the solidifying-point, whereas with spermaceti the melting-point is 0·4° C. lower than the solidifying-point. It has also been shown (Chemical News, cviii., 199) that the difference between the solidifying-point and melting-point of mixtures of stearic and oleic acid decreases and then increases as the softness increases. With tallows the difference between the solidifying-point and melting-point by this method amounts to 8° C. So far as the comparatively pure substances, stearic acid and spermaceti, are concerned the thermometer bulb method apparently yields results well within 1° C. of the true melting-point. This statement also holds good for mixtures of stearic and oleic acid up to 60 per cent oleic.

AN APPARATUS FOR THE PURIFICATION OF MERCURY BY DISTILLATION IN A VACUUM.

By Bertram Lambert.

The apparatus described below has been used very successfully for the purification of large quantities of mercury. It is simple in construction, rapid in action, and does no require any pump for exhausting it before use.

The figure shows the essential glass parts of the apparatus, which should be mounted firmly on a stand with some provision made for adjusting the height of the vessel M (see fig.).

The bulb A is of about 300 cc. capacity, and has a wide tube, B, sealed through its upper end as shown in the figure. This tube B is provided with a well-fitting rubber stopper, through which a narrow tube, D, passes to the bottom, and also with a side-tube, E. The lower half of the tube B should be thin-walled, and should be tapered slightly towards the closed end. This tube acts as a water cooled condenser for the mercury vapour, and the efficiency of the apparatus is greatly increased by having it as large as possible, and also as thin in the wall as is consistent with strength. A side-tube, F, is sealed into the bulb quite close to the junction between A and B. This tube should be bent up very steeply and drawn out to a capillary at the upper end.

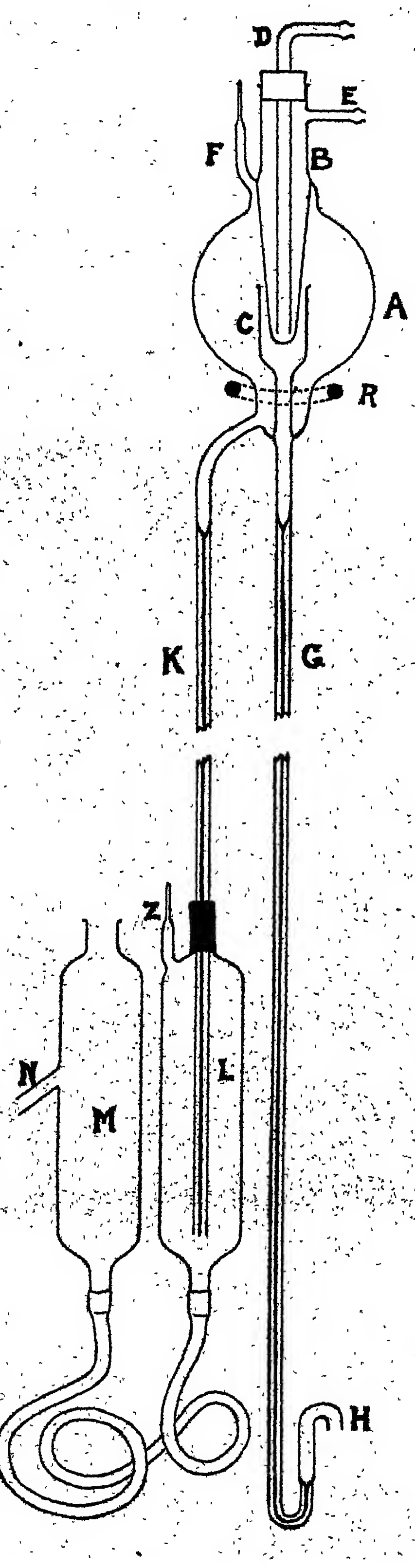
Into the lower end of the bulb is sealed a tube, G, which is widened out into a cup, C, at the top as shown in the figure. This cup is arranged so that its rim is just above the middle of the bulb A, the lower end of the condenser B being made to project about 3 cm. into it.

A side-tube, K, is sealed into the lower part of the bulb and bent, as shown in the figure, parallel to G. The lower parts of these tubes K and G are made from capillary tubing with a bore of about 1 mm. A wider piece of tubing is sealed on the end of G, which is bent as shown in the figure. The length from G to H should be about 760 mm.

The tube K is made to slide through the neck of the vessel L, and a good air-tight junction is made at the neck by means of stout rubber tubing. The vessel L, which is about 300 cc. capacity, is connected with a similar vessel, M, by means of a long piece of canvas-lined pressure-tubing. M is furnished with a side-tube, N, the use of which is described below.

The length from the middle of the bulb A to the middle of L should be about 760 mm.

Mercury is poured into M until M and L are about two-thirds full. It is convenient to have a drawn-out side-tube, Z, in the vessel L so that the air pressure can be adjusted during this operation. After the operation the point of Z is sealed. By raising M the mercury is made to rise slowly into the bulb A. It overflows into the cup C, and in order to prevent the escape of the mercury through G, the end H must be closed with a rubber cork. M is now raised further so that the mercury fills the bulb completely and rises into the drawn-out portion of the tube F. Care should be taken that no air-bubbles are trapped in any part of the bulb or cup. The capillary of F is now carefully sealed, while it is full of mercury, and the reservoir M is then gently lowered. The position of the reservoir M is adjusted so that the level of the mercury in the bulb A is about 5 mm. below the rim of the cup C. The point of the tube Z is



then cut off so that the air in L is kept at atmospheric pressure. A jar is now placed below H and the rubber cap removed. The mercury flows out from the cup C, displacing the air in the capillary G, and finally the difference in level between the mercury at G and H is the barometric height. If dry mercury has been used, and the above operations performed carefully, a very high vacuum will have been produced in the space above the mercury in the bulb.

Cold water is now made to flow through the condenser and the bulb heated, very gently at first, by means of a small ring-burner which is arranged as shown in the figure at R. An asbestos hood must be arranged round the bulb to protect it from draughts.

The mercury vapourises, is condensed on the cold tube B, and drops down into the capillary G. When sufficient mercury has been distilled to displace the mercury originally in G, the pure product can be collected. The drops of mercury falling into the capillary G act on the principle of the Sprengel pump, and maintain a very high vacuum in the bulb, removing the traces of air which enter the bulb dissolved in the mercury, and are then set free during the process of distillation.

The level of the mercury in the bulb will change with atmospheric pressure, and should be adjusted by altering the position of M. When the apparatus is working, mercury should be delivered into M through a fine jet at a rather faster rate than the mercury is distilling; by this means the level of mercury will be maintained in the bulb, the excess being collected at the overflow tube N. The apparatus can then be left working, without attention, for several hours.

The whole apparatus can be made from ordinary soft glass, and, if used carefully, will last many years. Care should be taken to heat the bulb gently, especially at first, and the flames from the burner should not be allowed to come into actual contact with the glass. Under such circumstances mercury can be distilled in the apparatus at the rate of about 3 lbs. per hour. The yield could probably be much increased by having the apparatus made from Jena glass or quartz and using a higher temperature, but there is no particular advantage to be gained. The purest product is got by slow distillation at as low a temperature as possible.

Mercury should be cleaned, by the usual methods, with 5 per cent nitric acid and thoroughly dried before distillation in the apparatus.

An extremely pure product may be obtained by frequent re-distillation, the apparatus being cleaned, washed, and dried between each operation.

The apparatus may be obtained from Messrs. A. Gallenkamp and Co., Ltd., Sun Street, Finsbury Square, E.C.

Chemical Department,
University Museum, Oxford.

INVESTIGATION OF MOLECULAR FORCES BY DISTURBANCE OF MOLECULAR EQUILIBRIUM IN LIQUID CRYSTALS.

By O. LEHMANN.

A SUBSTANCE is liquid if its elastic limit is zero, *i.e.*, if it cannot lastingly endure even the smallest elastic tension. There are many difficulties in the way of the practical determination of the elastic limit. The best method is as follows:—A plate of the substance under investigation is floated on mercury in a circular iron dish, in the middle of which there is a movable cylinder. The plate is attached to the walls of the dish and to the cylinder. The latter is caused to rotate by means of a string which is pulled with a force K. Equidistant radii are drawn on the plate. Within a certain circle of radius ρ the shearing force exceeds the elastic limit, and after a time it will be found

that within this circle the radii will be bent to form spirals, the effect being greater the longer the experiment lasts, while outside the circle there is only a very slight bending, which moreover disappears when K is removed.

As K is increased ρ also increases approximately proportionally, so that the graphic representation of the relation between ρ and K is a straight line through the origin, which however does not begin at the origin, but at a distance v from the K axis, if v is the radius of the cylinder. If $\rho = v$ the tension of the string is equal to the elastic limit, which may be denoted by K.

If we use an amorphous bituminous substance, the consistency of which decreases as the temperature rises, the graphic representations are straight lines which are more nearly perpendicular to the K axis the higher the temperature, corresponding to lower values of the elastic limit, which becomes zero at the temperature of liquefaction.

The actual performance of the experiment is rendered difficult by the fact that the temperature in the available space shows great variations, so that it is impossible to get a sharp demarcation between the region of perfectly elastic and that of persisting deformation. Other reasons may make such an experimental determination impossible, viz., the complicated composition of the bituminous mass, and the rarefaction of the mass, caused by tensile stress, in the neighbourhood of the circle ρ and its condensation in the neighbourhood of v.

It is still more difficult to investigate the existence of an elastic limit in crystalline substances in which the possibility of plastic deformation has been denied. I first observed true plastic deformation in ammonium nitrate, the five solid modifications of which are sotter the higher the temperature limits of their existence. From the graphic representations of the values of ρ it appears that the regular modification possesses no elastic limit, and that hence its crystals are not to be regarded as solid, but liquid.

It can easily be ascertained whether the substance is really crystalline or amorphous by allowing it to separate from a melt or solution. Only in the first case would single (anisotropic) individuals separate, which would grow and finally on coming into contact appear as fields of different orientation. On account of the difficulties already mentioned, it is usually impossible to determine whether the elastic limit of such a crystalline mass is zero.

In certain cases, however, these difficulties can be avoided, inasmuch as it is not necessary to carry out the experiments, but it may be deduced from the appearance of spontaneous homeotropism that the elastic limit must be zero. This spontaneous homeotropism is due to the replacement of the structure containing fields of different orientation by a simple anisotropic structure.

This process cannot be explained on the assumption that matter is continuous; it is a proof of the molecular hypothesis, and is moreover a new physical fact which cannot be deduced from existing molecular hypotheses, and demands an extension of them.

Spontaneous homeotropism excludes the existence of an elastic limit; for the elastic reaction force is caused by the molecules being distorted or pushed out of their position of equilibrium. Spontaneous homeotropism does not allow of the possibility of such an alteration of structure. If it occurred at a certain definite moment it would at once disappear (in consequence of spontaneous homeotropism) and the molecules would again become parallel of their own accord, and the cause of elastic reaction would thus be removed. It can be said with certainty that the confluent crystals of neutral ammonium oleate hydrate have no elastic limit and are liquid crystals.

It must be admitted that these liquid crystals have not a uniform structure like the model crystals of mineralogical collections. If even they possess a uniform structure at the moment of their formation, as is not improbable, inasmuch as the external form shows the existence of a dual axis of symmetry, this structure must be lost when they flow together. Hence I conclude that the individuals formed on flowing together no longer possess a dual axis of symmetry but a circular cross-section, and that they behave as if they consisted of leaflet shaped molecules (perpendicular to the optical axis), the surfaces of which readily become parallel to one another, while their edges are not parallel. Perhaps thermic movement is sufficient to make the orientation of the edges irregular and constantly changing, while it cannot prevent the surfaces remaining parallel. This molecular arrangement I called semi-isotropic (formerly pseudo-isotropic) because it is midway between the ordinary grating structure of solid crystals and the quite irregular molecular arrangement in amorphous liquids.

This semi-isotropic structure is homogeneous only in the case of relatively small individuals. Various discontinuities appear in larger masses, and the molecules arrange themselves so as to give rise to the formation of twin structures or fan structures.

All these structures, both homogeneous and discontinuous, are stable positions of equilibrium of the molecules, for they are re-established after disturbance by external forces. If thermodynamics (or rather the kinetic theory) did not require a continual energetic movement of the molecules, which cannot yet be demonstrated in liquid crystals by the Brownian movement of fine particles floating in them, we should imagine a state of static equilibrium of the molecules under the influence of electrostatic and electrodynamic forces. The difference between solid and liquid crystals must then depend upon the fact that in the latter the molecules can wander from place to place under the influence of thermic motion (if inequalities of this movement occur, such as are necessary for diffusion), while this is not possible for solid crystals, or at any rate not unless a strain exceeding the elastic limit is exerted on them.

In the latter case, for example, when a prismatic crystal is bent, the wandering of the molecules causes the decrease (relaxation) of the elastic tension, and the grating structure is destroyed. When a liquid crystal of ammonium oleate is bent in consequence of spontaneous homeotropism the elastic tension disappears completely and the structure becomes fan-like. A state of perfect molecular equilibrium is not reached, for such bent liquid crystals are only observed momentarily, where the hydrodynamic force compels them to follow curved lines of flux, or where they become attached to the glass. When floating freely they spontaneously assume their normal form, like each fragment resulting from the destruction of an individual. With liquid crystals the equilibrium of the molecules extends not only to the structure but also the form. It is doubtful whether capillary pressure and expansive force come into play, and there is much uncertainty about the nature of molecular equilibrium and the forces which condition it. It seems to me that the first task of molecular physics is to examine the nature and action of these forces. The same method which was used for non-molecular forces, the disturbance of the state of equilibrium by known external forces, may lead to the desired result.

A case of this kind is the disturbance of molecular equilibrium by mechanical forces. If the plate in the torsion apparatus previously described were a liquid crystalline mass, and the rotation of the cylinder exceeded a certain speed, in accordance with previous observations of induced homeotropy, the axes of the molecules in the neighbourhood of the cylinder would all become parallel to the axis of rotation. Thus in a ring-shaped region a semi-isotropic structure would be established, the direction of the optical axis coinciding with that of the axis of the cylinder. The molecules behave like furniture castors, the axes about which they turn most easily being perpendicular to the direction of push. And just as on pushing a wheelbarrow fitted with castors the resistance to pushing decreases as soon as the castors have arranged themselves properly, the disc-shaped molecules, when arranged parallel to the plane of rotation, act like friction wheels so that the internal friction is lowered. The limit

of the semi-isotropic region is the place where the shearing force exceeds the molecular directing force. The latter can be ascertained by quantitative experiments of this kind.

By pressing the liquid crystalline mass between two glass plates the optical axes are made parallel to the glass, *i.e.*, the surfaces of the molecular leaflets are parallel to the glass. In very thin layers, or in narrow capillary tubes, the adsorption power of the glass acts in the same way. If the mass is made to flow through such tubes at moderate velocities, the interference bands remain unchanged in polarised light. Hence we may deduce that the molecules cannot be little rods, for then, since the rate of flow is greater round the axis of the tube than near the walls, they would arrange themselves obliquely if they were originally perpendicular to the glass. Leaflets, on the contrary, would easily glide over one another without losing their parallelism. As a matter of fact, a liquid crystalline mass between two glass plates can be made semi-isotropic in such a way that the optical axes are perpendicular to the glass while the plates are slowly pushed over one another. If the rate of flow in the capillary is greater in the neighbourhood of the axis forced, homeotropism must appear, the axes of the molecules turning through 90°. Here, also, quantitative experiments would give the molecular directive force.

Another case of the disturbance of molecular equilibrium is that caused by contiguous anisotropic plates, but here the acting force is not known.

Observations of the disturbance of equilibrium by magnetic forces which could easily be graduated would be of special value. Powerful surface tensions, such as for example appear at the surface of liquid crystals and air, might also disturb the arrangement of the molecules, in that they would compel the molecular leaflets to arrange themselves parallel to the surface. As the surface tension towards the mother-liquor is readily altered by suitable additions, there is a possibility of quantitative determinations. The most striking case is that of disturbances of molecular equilibrium by foreign substances which can form mixed crystals with the liquid crystals, and also the cases of swelling up in water and other liquids. The growth of myelin forms (of crystals of neutral ammonium oleate hydrate rich in water) and the apparently living crystals of parazoxycinnamic acid ethyl ester from monobromnaphthalene (which contain solvent) depend upon the same phenomenon. The direct cause is partly decrease of capillary pressure where the swelling up occurs and partly the crystallisation force.—Abridged from *Verhandlungen der Deutschen Physikalischen Gesellschaft*, xv., No. 10.

RECENT WORK IN INORGANIC CHEMISTRY.*

By JAMES LEWIS HOWE.

Elements.—A very complete investigation of the precipitation of silver on glass in mirror form has been made by Kohlschütter (*Ann.*, ccclxxxvii., 86). The solution used was ammoniacal silver nitrate with some reducing agent such as formaldehyde, grape sugar, milk sugar, tartaric acid, hydrazine, and others. In the solution very little silver is present as Ag^+, but there is a relatively large number of OH^- ions. The precipitation of silver in mirror form depends upon the very slow oxidation of the reducing agent, silver oxide being the oxidising agent, and the concomitant formation of substances of high molecular weight or of colloidal form, everything which antagonises sol-formation being unfavourable to mirror formation. The character of the mirror is greatly influenced by the composition of the silvering solution and also by the character of the glass upon which the mirror is precipitated. The reason for the precipitation of the silver on the glass is that the silver hydroxide is adsorbed by the glass (hence the influence of the kind of glass), and the reducing agent must also be adsorbed by the glass. Thus everything that affects the surface tension of the solution affects the mirror. Microscopic and ultramicroscopic examination shows that the silver is amorphous and homogeneous, and it may be considered to be in a state of colloidal division. Thus while the mirror is unchanged by alkalis, it is easily removed by very dilute acids, though not dissolved. The sudden appearance of electrical conductivity in the mirror and its rapid increase are explained by the precipitate being laid down in discrete particles which in time bridge over the intervening spaces. The increase in conductivity of the finished mirror corresponds to the spontaneous coagulation of a metal-sol, while the increase under the influence of acids corresponds to the electrolytic precipitation of the sol. The mirror formed by the cathodic dusting of silver in dilute gases varies in character with the gas used, as does the precipitated mirror with the solution.

The rapidly increasing use of many of the rarer metals has led to fuller investigation of their properties. Efforts to get a pure vanadium have been made by Ruff and Martin (*Zeit. Angew. Chem.*, xxv., 49), but without complete success. Previous attempts to reduce the easily fusible V_2O_5 to metal having been unsuccessful, V_2O_3, which fuses at 2000°, was reduced by aluminum, as well as by carbon and vanadium carbide. The best product obtained was nearly 99 per cent pure. The difficulty of getting a pure metal lies in the fact that the vanadium dissolves the oxide VO, as well as aluminium and carbon, hence no latitude in proportion of reducing material is permissible, and the whole mass must react uniformly, conditions practically impossible of attainment. The melting-point of the pure metal was calculated as 1715° and the density as 5·688. Brunck (*Chem. Ztg.*, xxxvi., 1233) suggests the use of tantalum as material for electrodes, especially for analytical purposes. For cathodes tantalum can only replace platinum, being lighter, firmer, insoluble in aqua regia, without tendency to alloy with zinc and cadmium, cheaper, and is not attacked in the electrolysis of alkalis. Alone, it cannot be used for anodes, as it quickly becomes coated with a very thin but non-conducting layer of oxide (probably Ta_2O_4), but tantalum anodes which are very thinly plated with platinum serve every purpose. Tantalum has also been suggested as a superior material to platinum for accurate weights. Ruder (*Journ. Am. Chem. Soc.*, xxxiv., 387) has described the solubilities of malleable tungsten and molybdenum, and finds the former very slightly attacked by any acids or alkalis in solutions, though dissolved by fused alkalis. A saturated solution of sodium hypochlorite attacks it slowly and it is dissolved by a mixture of nitric and hydrofluoric acids, but not by chromic acid mixture. Molybdenum, on the other hand, presents little resistance except to hydrofluoric acid and alkali solutions. It is more readily dissolved by dilute than by strong acids. In a paper before the Section of Electrochemistry at the Congress of Applied Chemistry the properties and applications of ductile tungsten are very fully described. Among possible laboratory applications in replacing platinum are resistance furnaces, filtering gauze, acid-proof dishes and tubes, and analytical weights. The volatility of the metals of the platinum group, under conditions which appertain in the analytical laboratory, has been studied by Sir William Crookes (*Proc. Roy. Soc. London*, (A) lxxxvi., 461) using an electric resistance furnace as a source of heat. At 900° platinum is not volatile, but at 1300° it loses in two hours 0·019 per cent and in thirty hours 0·245 per cent. This would mean a loss of weight of 24·5 mgrm. from a 10 grm. crucible. The loss is due to sublimation, the sublimed metal being deposited in hexagonal flakes with metallic lustre. Iridium proves to be decidedly more volatile, losing 0·030 per cent in two hours and 0·092 per cent in twenty-two hours at 900°, while at 1300° the loss in two hours is 0·828 per cent and in twenty-two hours 7·297 per cent. Between 100° and 1400° the loss is pro-

* *Journal of the American Chemical Society*, xxxv., No. 2.

portional to the temperature. The loss is due to the formation of a volatile oxide. Rhodium suffers no change in weight at 900°, even after eight hours heating, and at 1300° loses but 0·021 per cent in four hours and 0·131 per cent in thirty hours. It is thus the least volatile of the metals of the group. Ruthenium at 1300° loses 25 per cent of its weight in eight hours, and this is attributable to the formation of an oxide. The reviewer may add that on heating ruthenium in a current of air in an ordinary combustion furnace the odour of RuO_4 is very distinct, and a lower oxide sublimes on the inside of the tube and on the porcelain boat containing the metal. The boiling-point of a number of metals at atmospheric pressure has been obtained by Greenwood (*Zeit. Elektrochem.*, xviii., 319), using a carbon crucible hung in a carbon tube which served for electrical heating, and determining the temperature of distinct boiling by a Wanner pyrometer. For those metals which are attacked by carbon a graphite crucible with fused magnesia lining was used. The following boiling-points were found:—

Mg 1120° Sb 1440° Al 1800° Ag 1955° Sn 2275° Fe 2450°
Bi 1420° Pb 1525° Mn 1900° Cr 2200° Cu 2310°

The boiling-point curves for other pressures are shown in curves but the figures are not given.

The action of metals on fused alkalis has been continued by LeBlanc and Weyl (*Ber.*, xlv., 2300), and the results obtained with potassium hydroxide are found to be in many respects very different from those with sodium hydroxide. While sodium decomposes NaOH quantitatively at 450° with evolution of H and formation of Na_2O, K is without action on KOH even at 550°. When Na acts on KOH there is weak evolution of H, and K volatilises. With K on NaOH some H is given off but no metal. Evidently an equilibrium, $K + NaOH \rightleftharpoons Na + KOH$, is soon attained and then the Na acts on the NaOH. Al has no action on KOH, but it acts on NaOH moderately with evolution of H and H_2O. Cr, Mo, and W act on KOH slowly with evolution of H and formation of chromates, molybdates, and tungstates and some evolution of K. The reactions appear to be—

$$6KOH + M = M(OH)_6 + 6K,$$
$$M(OH)_6 + 2KOH = K_2MO_4 + 4H_2O,$$
$$4H_2O + 4K = 4KOH + 2H_2.$$

With C there is evolution of H, formation of K_2CO_3 and some K. The K appears to have no action on the K_2CO_3. With Mg there is evolution of H with KOH and precipitation of MgO, while with NaOH, Mg gives off both H and H_2O. With Si the reaction is violent and the formation of SiO_2 quantitative, but the H given off is somewhat less than the expected 4H for each atom of Si. With Ni, Co, and Fe there is no evolution of H or H_2O from KOH (as there is from NaOH), but the metals are attacked with the formation of a small amount of oxide. In general KOH is much more stable than NaOH.

In 1910 it was found by von Bolton that hydrocarbons were reduced by alkali-amalgams to carbon, a part of which appeared to be in the form of diamond. Utilising the fact that crystallising substances have a strong tendency to be deposited on crystals of the same substance if present, von Bolton (*Zeit. Elektrochem*, xvii., 971) led moist illuminating gas for four weeks through 14 per cent sodium amalgam in a tube coated with a very fine suspension of diamond powder in water-glass. The whole was kept at 100°. Under the microscope the powder was apparently amorphous, but after the experiment minute crystals were clearly visible. These showed the properties of diamonds, and while the quantity did not suffice for quantitative analysis it seems extremely probable that diamonds are thus formed by the reduction of hydrocarbons. Two important papers on ozone have appeared during the year, one by Harries (*Ber.*, xlv., 936) and one by Traube (*Ibid.*, 2201). The former finds that by the action of ozone on symmetrical butylene four products may be formed. When the ozone has been previously led through NaOH and H_2SO_4, there are formed a monomeric ozonide, $C_4H_8.O_3$, which can be distilled in a vacuum, and a dimeric form, $(C_4H_8.O_3)_2$, which is not volatile. If the ozone is not previously purified, two similar products are obtained but with the formulæ $C_4H_8.O_4$ and $(C_4H_8.O_4)_2$, which Harries calls oxozonides. Similar products are formed with other hydrocarbons containing a double bond. From these experiments Harries concludes that ordinary 11—14 per cent ozone is made up of about two-thirds ozone, O_3, and one-third oxozone, O_4, and that the latter is largely destroyed by leading it through alkali and acid, though the purified ozone still contains a little oxozone. Traube's experiments deal with the action of ozone on solid KOH. A red compound is formed which resembles in appearance $K_2Cr_2O_7$, and which decomposes in water or acids, giving off oxygen, chiefly as O_2, but with some O_3, while the solution contains some H_2O_2. On standing or heating, this red compound loses its colour and the white product decomposes with formation of H_2O_2 and evolution of oxygen. It is evident that the red product is a higher oxide, probably K_2O_7, which Traube calls potassium ozonate, but it contains some proportion of a lower oxide and also unchanged KOH. The oxide which is present with it and into which it decomposes on standing is doubtless the tetroxide, K_2O_4, since like this it gives H_2O_2 and oxygen in approximately molecular proportions. As Traube's ozone was passed over concentrated H_2SO_4 before absorption, no evidence appeared of the presence of oxozone.

The possible action of pressure in causing chemical reactions in the metamorphosis of minerals was several years ago suggested by Van Hise, and this has led to an experimental examination of the subject by Spezia (*Atti Accad. Sci. Torino*, xlvi., 19). By using pressures of 6000 to 9500 atmospheres, corresponding to depths of 20 to 30 kilometres, and in some cases continuing the pressure for several months, no instance of chemical action could be found. No action took place between silica and calcite, indicating no silicification. Alabaster, alum, and limonite, embedded in pulverised quartz for eight months at a uniform pressure of 8000 atmospheres, showed no loss of water. The great difference between the action of heat and of pressure was shown by the fact that goethite, heated in water to 330° for seven days, became anhydrous, while it remained unchanged under 9500 atmospheres pressure continued for twenty-six days. To test reduction, CuO was kept in contact with magnesium and then with potassium for months at 9500 atmospheres pressure without change, although the sum of molecular volumes would have been decreased by a reaction; nor was calcite changed to arragonite. Bismuth was not liquefied by a pressure of 9000 atmospheres. *A propos* of plasticity under pressure, Spezia calls attention to the great difference between one-sided pressure and a pressure uniform on all sides; the latter alone cannot liquefy metals nor plastic substances.

Bergius (*Zeit. Elektrochem.*, xviii., 660), working on reactions under pressure, finds that when peat is heated in water to 250—350° it is charred, and from the velocity of the reaction he considers it possible to calculate the time necessary for bituminous coal formation in nature. His calculations place the time at seven to eight million years, which he considers agrees with geological estimates.

Group II.—According to Bleyer and Müller (*Zeit. Anorg. Chem.*, lxxv., 285) from the chemical nature of glucinum it would be expected that compounds of glucinum and arsenic acid would be strongly hydrolysed, yet that in them the glucinum and the acid would be in a definite molecular ratio. This was confirmed experimentally, and tri-glucinum salts obtained when the di-glucinum would be normal, and basic salts where tri-glucinum would be called for. Thus disodium arsenate precipitated tri-glucinum arsenate from glucinum

sulphate, and trisodium arsenate a monobasic salt, $Gl_3(AsO_4)_2\ GlO.8H_2O$. Monoglucinum arsenate, $Gl(H_2AsO_4)_2$ and the di-glucinum salt, $GlHAsO_4$, were prepared by dissolving the calculated quantity of glucinum hydroxide in arsenic acid. The ammonium salt, $NH_4GlAsO_4.4 \cdot 5H_2O$ was fairly stable but the other alkali salts were basic, and the hydrolysis became greater on allowing the salt to stand in its mother-liquor. Except the monoglucinum arsenate, which consisted of hygroscopic crystal-flakes, all the compounds were amorphous. The behaviour of glucinum with arsenic acid seems thus to be somewhat similar to that with phosphoric acid, though the glucinum phosphates have not been worked out with sufficient definiteness to show a clear analogy.

(To be continued).

A STUDY OF CERTAIN CONFIRMATORY TESTS FOR TIN.

By LOUIS J. CURTMAN and MAX MOSHER.

I. *The Iron Nail Reduction Test followed by Treatment with Mercuric Chloride.*—This well-known test for tin, which consists in reducing the stannic chloride in acid solution with iron and subsequently treating the stannous chloride formed with mercuric chloride, was proposed by A. H. Allen in 1872 (*Journ. Chem. Soc.*, xxv., 274). It is mentioned in nearly every text-book on qualitative analysis. Despite its general use, nothing very definite appears to be known concerning the conditions under which this test may be relied upon to give constant results. The frequent failure of students to report this metal indicated the need for further investigation. It was therefore the object of this work to ascertain the best conditions for this test, and also to determine its limit under these discovered conditions.

The standard solution employed throughout this work was prepared in the following manner:—Ten grms. of chemically pure tin foil were treated in a 500 cc. Erlenmeyer flask with an excess of hydrochloric acid (sp. gr. 1·19), and solution was hastened by heating on a steam-bath. The solution was saturated with chlorine to completely oxidise the tin to the stannic condition. It was then boiled for some time to expel the last traces of free chlorine as well as to reduce the quantity of hydrochloric acid present. After cooling, the solution was diluted to 500 cc. in a volumetric flask. A portion, thoroughly mixed, failed to react with a saturated mercuric chloride solution, showing that all the tin was completely oxidised.

To determine whether any stannic chloride had been lost by volatilisation while the excess of chlorine was being boiled off, the solution was analysed for tin by the method given by Treadwell ("Quant. Anal.," trans. by W. T. Hall, p. 243). Two well agreeing determinations made on 20 cc. portions of the solution gave as the average result 19·9 mgrms. Sn in 1 cc.

To determine the quantity of free hydrochloric acid in the solution, separate portions of it were titrated with standard potassium hydroxide solution, by the method described by Treadwell (*Ibid.*, p. 495). The acidity was found to be 0·0063 grm. of anhydrous hydrochloric acid per cc., which, in the diluted solutions used in the tests, was reduced to such an extent as to be neglected without any appreciable error (Note 1).

This solution was not used directly, but 100 cc. of it were diluted with an equal quantity of water, giving a solution of 9·95 mgrms. Sn in 1 cc. In nearly all the sets of experiments performed the largest volume used was 0·5 cc., equivalent to 4·97 mgrms. Sn. This is practically 5 mgrms. Sn, and was so assumed in all experiments, for the reason that the error resulting from this assumption is too small to be detected by this test, as will be shown later. The smallest volume of this solution used was 0·1 cc. containing 0·995 mgrm. Sn, which for the reason stated above was considered 1 mgrm. When smaller quantities of tin were required, a portion of the second solution was again diluted so that 1 cc. was equivalent to 0·1 mgrm. Sn. In this dilution it was found that hydrolysis took place very rapidly; to prevent this, a new solution of similar strength was prepared, to which was added 5 cc. of concentrated hydrochloric acid to every 50 cc. (Note 2). This proved to be satisfactory.

The general procedure was as follows:—To definite amounts of concentrated hydrochloric acid pipetted into test-tubes were added varying quantities of a standard tin solution. After dilution to 5 cc. one or two nails were added, the tubes placed in a boiling water-bath (Note 3), and the reduction was allowed to continue for from two to five minutes; the contents of the test-tubes were then immediately filtered into 2 cc. of saturated mercuric chloride solution. The filtrates were examined after five minutes and the results recorded. In all cases where less than 1 mgrm. of tin was used the results were controlled by one, two, or even three blanks. This was necessary because it was found that under certain conditions a cloudy filtrate was obtained from the blanks. To determine whether this cloudiness in the blank was due to an interaction between a substance resulting from the action of the acid on the iron and the mercuric chloride, the following experiments were performed:—In separate test-tubes, one, two, and three 1¼-inch cut nails were heated for five minutes with 5 cc. of hydrochloric acid (1—1) in the boiling water-bath, and the solution was then filtered into distilled water. The water in each case became slightly cloudy. The experiments were repeated except that the reaction product was filtered into mercuric chloride instead of distilled water. The same results were obtained, showing that the cloudiness was due to very fine particles of carbon which passed through the filter.

It was the object of the first experimsnts to determine the effect of heating for two minutes in the presence of a one-quarter inch brad in a volume of 5 cc. containing 2 cc. (1—1) HCl.

The results of sixteen experiments with diminishing amounts of tin under these conditions showed that with 1 mgrm. of tin the results were inconsistent, the final results of three tests being a fair cloud in the first case, a faint cloud in the second case, and a practically negative result in the third. In two tests where 2 mgrms. of tin were used, the results were also discordant. Prolonging the time of heating as well as increasing the concentration of the acid did not give uniform results. It was, however, observed that in every series of experiments the reducing action in the water-bath was not uniform. As the conditions in each set of experiments were kept constant, it appeared that the irregular results obtained were due to a lack of uniformity in the nails employed. To test this point, four blank tests were run under the conditions mentioned for the first tests, with one and one-quarter inch brads selected at random. The action in the water-bath was decidedly not uniform. At the conclusion of three minutes the acid was poured off. The nails were then washed, treated with fresh acid, and again subjected to the same tests. This was done to see whether the first treatment had eliminated any differences which might be due to variations in the surfaces of the brads. The action of the acid during the second treatment was also not uniform. Finally, the brads were examined, and it was found that the acid had so energetically attacked one of them that it was about one-half the diameter of any of the others. These results verified the conjecture that the inconsistencies in the previous tests were due to the variations in the iron nails which caused the stannic chloride to be reduced at different rates in the water-bath.

The brads employed in these preliminary tests were therefore rejected, and the previous experiment was repeated with one and one-half inch wire nails. The results were also found to be very irregular. Accordingly, one and one-half inch cut nails, or four-penny nails, were used. These gave uniform results, and were employed in all further experiments, unless otherwise specified. The

results of all further tests were classified as good or negative; good when they could readily be distinguished from the blanks run at the same time, negative in all other cases.

Having found nails to act with a fair degree of uniformity, it was the purpose of the next series of experiments to determine the separate and combined effects of the various factors which influenced the delicacy of the test. These are, first, the acid concentration; second, the time of heating; and, third, the number of nails employed. As a result of a large number of experiments, the conditions which were most favourable for the test were found; these, together with the results obtained in the final tests, are given in Table I. Under the conditions stated the results show that the smallest quantity of tin which may be detected is 0·2 mgrm. in a volume of 5 cc. The blanks obtained were practically perfect, and the results of the limit tests were very striking when compared with the blanks run at the same time. Under no circumstances could the results be mistaken.

To determine whether two nails would not give better results under the conditions of the tests in Table I., another series of experiments was performed as given in Table II. The blanks in these tests were not so good as those obtained under the conditions as in Table I. The results therefore were not so striking and conclusive. The conditions for the test as given in Table I. are therefore to be preferred.

As increasing the number of nails did not improve the test, it was thought worth while to see if prolonging the time of heating to five minutes would not give better results. To this end the experiments given in Table III. were made. The results show that extending the time to five minutes does not increase the sensitivity of the test.

Before concluding this work it was thought desirable to carry out one more set of experiments in which the conditions given in Table I. were varied both as to the time of heating as well as to the number of nails employed. The results are embodied in Table IV. The results show that the sensitivity of the test under these conditions is greater than that given in Table III.; the limiting test is, however, the same as that given in Table I. There is, however, an important difference in the quality of the blanks obtained under these different sets of conditions, and correspondingly in the decisiveness of the results. The blanks obtained under the conditions of Table I. are clearer, and as a consequence the limit tests are more readily distinguished than those of Table IV. The conditions given in Table I. are therefore to be recommended.

Influence of Antimony on the Test.—Having determined the best conditions for the iron-nail reduction test for tin when this metal alone is present, it was desirable to ascertain whether these conditions would hold good in the presence of antimony, for in most schemes of analysis the test for tin is made in the presence of antimony. Since the maximum amount of this metal in any given solution seldom exceeds 500 mgrms., and since it is customary to divide the solution containing antimony and tin into two equal portions before testing for each of these metals, 250 mgrms. of antimony (Note 4) were employed in each of the tests given in Table V. The conditions are the same as those which are afforded the maximum delicacy of the test when tin alone was present (see Table I.).

To control the results of Table V., two sets of blanks were run; one of the usual kind containing neither antimony nor tin, and the other containing only antimony. The latter were perfectly clear, and thus facilitated the detection of small quantities of tin; the former were practically clear, and could readily be distinguished when compared with the tubes containing tin. Comparison of the tubes is best made by holding them at arm's length against a dark field, such as the floor. The difference can then be very readily seen.

All the blanks which might contain any unreduced antimony were largely diluted. No precipitate formed, indicating that even after reduction there was enough free acid present to keep the antimony in solution, thus obviating the danger of mistaking a precipitate of antimony oxychloride for the test for tin.

Table I.

(Time of heating, three minutes. Acidity, 2·5 cc. concentrated HCl. Volume, 5 cc. One 1½ in. cut nail).

No.	Sn (mgrms.).	Result.
1—13	20·0—1·0	Good
14—18	0·5—0·3	Good
19—26	0·2	Good
27—29	0·1	Negative

Table II.

(Conditions same as those of Table I., except that two 1½ in. cut nails were used instead of one).

1—12	3·0—0·3	Good
13—14	0·1	Negative

Table III.

(Conditions same as in Table I., except that the time of heating was increased to five minutes).

1—14	3·0—0·3	Good
15—18	0·2—0·1	Negative

Table IV.

(Time of heating, five minutes. Acidity, 2·5 cc. concentrated HCl. Volume, 5 cc. Two 1½ in. nails).

1—13	0·1—0·2	Good
14—18	0·1	Negative

Table V.

(Time of heating, three minutes. Acidity, 2·5 cc. HCl (Note 5). Volume, 5 cc. One 1½ in. cut nail).

N	Sn (mgrm.).	Sb (mgrms.).	Result.
1—8	20·0—0·3	250	Good
9—12	0·2	250	Good

Summary and Conclusions.

1. That certain nails are unsuitable because of the irregularity of their action.

2. That in a total volume of 5 cc. with one 1½ inch cut nail the best conditions are:—Time of heating, three minutes in boiling water-bath; acidity, 2·5 cc. concentrated HCl.

3. That under these conditions the smallest amount of tin that can be detected either alone or in the presence of 250 mgrms. of antimony is 0·2 mgrm. in a volume of 5 cc.

4. That it is imperative to run a blank when the quantity of tin present is small.

II. Instead of reducing the tin with an iron nail, some analysts prefer to reduce the tin to the metallic state by means of zinc in an acid solution, and then test the solution of the precipitated tin in hydrochloric acid with mercuric chloride. This test has recently been investigated by Noyes and Bray (*Journ. Am. Chem. Soc.*, xxix., 181), who found that it possesses a delicacy of 0·5 mgrm. Our experiments confirmed their work.

III. *The Test Based upon the Reduction of Ammonium Molybdate.*—This test was first proposed by Longstaff (Chemical News, lxxx., 282), who states that it is delicate to 1 part in 1,500,000 when directly applied to a freshly prepared stannous solution. In the application of this test to qualitative analysis Baskerville finds that it is easily sensitive to 1 part of tin in 5000 (*Journ. Elisha Mitchell Scientific Society*, Feb., 1900, xvi., Part II.). As diligent search of the literature failed to disclose a record of systematic experiments performed to establish the conditions which would afford the greatest delicacy to the test when applied to stannic solutions as the starting point, the following work was undertaken. In our work, stannic solutions were exclusively employed, for the reason that it is in this form that tin is encountered in the course of systematic analysis.

TABLE VI.

(Total quantity of acid, 4 cc. Two cc. added each time).

No.	Sn (mgrm.).	Result.
1	1·0	Fair blue
2	0·2	Faint blue
3—4	0·1 – 0·05	Negative

TABLE VII.

(Total quantity of acid, 3 cc. Two cc. added first time. One cc. added second time).

1	0·1	Faint blue
2—4	0·05—0·03	Very faint blue
5—6	0·02—0·01	Negative

TABLE VIII.

(Total quantity of acid, 2·5 cc. 1½ cc. added first time. One cc. added second time).

1—2	0·1 —0·05	Faint blue
3—6	0·04—0·01	Very faint blue

TABLE IX.

(Same conditions as in Table VIII.).

No.	Sn (mgrm.).	Sb (mgrms.).	Result.
1—4	1·0 —0·4	250	Good blue
5—6	0·3 —0·2	250	Fair blue
7—10	0·1 – 0·08	250	Faint blue
11—12	0·05	250	Very faint blue
13—16	0·04—0·02	250	Negative

TABLE X.

(Quantity of Sn, 1 mgrm.).

No.	Final acidity (cc.).	Result.
1	2·5	Dark blue
2	3·0	Lighter blue
3	3·5	Still lighter blue
4	4·0	Fair blue
5	4·5	Faint blue
6	5·0	Colourless or negative

The method of reducing the tin with an iron nail in acid solution was found inapplicable, because of the reducing action of the ferrous salt, formed in the reaction, upon the ammonium molybdate. Accordingly, reduction by means of zinc was tried.

After a number of preliminary experiments the following procedure was finally adopted:—To definite amounts of concentrated hydrochloric acid run into test-tubes from a burette, varying quantities of standard stannic chloride solution were added, and the volume was then made up to 5 cc. After the addition of a scant one-half grm. of chemically pure granular zinc (Note 6), the tubes were put into the boiling water-bath, and allowed to remain therein until the action practically ceased; another definite quantity of concentrated hydrochloric acid was then added (Note 7). As soon as the second reaction was completed (Note 8), the solution was diluted to 10 cc., and immediately filtered into 1 cc. of saturated ammonium molybdate solution. The results were immediately compared with a blank run simultaneously.

In the above series of experiments the total quantity of acid used in the test was gradually reduced in order that the best conditions of acidity might be found. The results are given in Tables VI., VII., and VIII.

A comparison of the results of these tables shows that the conditions given in Table VIII. are the best, since the test becomes delicate to one part in a million. The blanks obtained throughout the work were found to possess a slight greenish blue colour which could readily be distinguished from the pure faint blue of the limit test.

Influence of Antimony upon the Test.—Having determined the most favourable conditions for the test when tin alone is present, the next step was to ascertain the influence of the presence of antimony on the test under these conditions. For reasons given earlier in this paper, 250 mgrms. of antimony were used. The results are given in Table IX. These results show that the sensitivity of the test is lowered by the presence of large quantities of antimony, and that under these conditions the limit is 0·05 mgrm. Sn.

Having found the test to work satisfactorily in the presence of the maximum amount of antimony, it was thought desirable to ascertain the influence of small quantities of this metal. The results of these tests showed that under the conditions given in Table VIII., 0·03 mgrm. of tin could be detected in the presence of 10 mgrms. of antimony, and that quautities of antimony up to 5 mgrms. are without influence on the test.

Longstaff states that an excess of acid vitiates the test by discharging the blue colour, but supplies no experimental data on this point. As some preliminary work on our part had shown this statement to be true, it was thought worth while to run a series of experiments with the object of establishing definitely the influence of acidity on the test. In these experiments the regular procedure already given was followed, except that the quantity of acid added was varied in order to yield different acid concentrations after dilution to 10 cc. The results obtained are given in Table X.

These results definitely show the influence of acidity on the delicacy of the test, and demonstrate the necessity for keeping the acidity within 4·5 cc. if a trustworthy test for 1 mgrm. of tin is desired.

Summary and Conclusions.

The investigation of the conditions under which the ammonium molybdate test for stannous tin might be applicable to stannic solutions after reduction by zinc showed:—

1. That with a total acidity of 2·5 cc. of concentrated hydrochloric acid in a volume of 10 cc., the acid being added as directed, the test is delicate to 0·01 mgrm. Sn in the absence of antimony.

2. That in the presence of 250 mgrms. of antimony the test can be used to detect 0·05 mgrm. of tin.

3. That the presence of 5 mgrms. of antimony is without influence on the delicacy of the test.

Notes.

1. Upon dilution to 1—1 the amount of free acid becomes 0·0031 grm. per cc., which in consideration of the final acidity of the solutions employed in the tests, may be neglected without any appreciable error, particularly so since the volume of the standard tin solution used never exceeded 1 cc.

2. As the volume of this tin solution employed in any test never exceeded 0·5 cc., the quantity of additional acid was 0·05 cc. This amount, when compared with the quantity added in any test is so small as to be neglected without any apparent difference in the result.

3. The water-bath employed throughout this work consisted of a 500 cc. beaker half filled with water, and covered with a lead plate having six perforations large enough to accommodate the ordinary size of test-tubes. The water was heated to boiling in each case before inserting the tubes, and the boiling thereafter continued for the full time that the tubes were in the bath. This form of water-bath was found very convenient in this work, since it enabled us to perform six tests at one time. The glass beaker was preferred to the usual copper-bath, for the reason that the former permitted us to observe the progress of the reaction.

4. The solution used was made by dissolving 18·8 grms. $SbCl_3$ in HCl (1—1), and making the volume up to 100 cc.

in a volumetric flask by the addition of more HCl (1—1). The strength of this solution was 100 mgrms. Sb in 1 cc.

5. The 1·25 cc. concentrated HCl contributed by the antimony solution is included in this total of 2·5 cc.

6. A very granular form of zinc reduced the time of the reaction by reason of its readiness to dissolve in the acid.

7. In the above procedure the acid was added in two portions, the first to aid in the reduction of the tin by the zinc, and the second to re-dissolve the spongy tin which separated out. This method gave a rapid solution of the tin. If instead of adding the acid in two portions as just described, the total quantity was added at the outset, it was found that the tin did not readily go into solution on further heating.

8. In a few of the many experiments tried, an intense blue coloration was obtained, which was out of proportion to the small quantity of tin present. These results were due to the presence of minute particles of metal which passed through the filter. Hence care must be exercised in filtering.—*Journal of the American Chemical Society*, xxxv., No. 4.

THE PHYSIOLOGICAL PRINCIPLES OF HEATING AND VENTILATING.*

By Professor LEONARD HILL, M.D., F.R.S.

Lecture II.—Radiant v. Convected Heat.

The lecturer began by again insisting on the enormous importance of certain kinds of dust in the atmosphere. Workers in limestones have little more phthisis and respiratory disease than the general run of males, while those who work in sandstones and any process which generates silica dust, suffer very greatly and have a shorter prospect of life. The disease and the increased mortality which arises from lead and silica dust can easily be prevented, and must be prevented. He then went on to detail the experiments which prove that there is no organic poison in exhaled air, and that the increased percentage of carbonic acid and diminished percentage of oxygen in the air of crowded rooms had nothing to do with the symptoms of discomfort felt therein.

Prof. Hill then dealt with the physical conditions of the atmosphere, the heat, moisture, and movement, which he said profoundly affected the health and vigour of the body. Wrong physical, not chemical, conditions of the atmosphere cause all the discomfort of crowded rooms.

Body heat (its production and its diminution) was discussed, and the effects of body heat stagnation described. It was pointed out how a warm still atmosphere depresses the activity of the body, the oxygen intake, and the vigour of the circulation, together with the appetite for and digestion of food.

The importance of cutaneous sensations and the depressing effect of monotony of atmospheric conditions were brought into prominence. A new instrument for measuring the rate of cooling, the Kata-thermometer, was described, and the failure of the ordinary thermometer to indicate the proper conditions for body comfort and health illustrated. Observations taken with the Kata-thermometer in and out of doors at the seaside were mentioned. The natural conditions on ideal summer days were described, and the advantages of radiant heat and cooling moving air insisted on. The wastefulness and the pollution of the atmosphere by the open fires impelled us towards the use of the modern gas fire, which gave 50 per cent of the energy of the fuel as radiant heat. Artificial heat, and particularly air heated by convection, was not good for us, and ought always to be associated with open windows.

* Chadwick Public Lectures, Bristol, 1913. (Delivered at Bristol University, October 30. The Lord Bishop of Bristol in the Chair)

THE SCIENTIFIC WEEK.

(*From Our Own Paris Correspondent*).

Seven Grms. of Radium in the Whole World!

A quite recent census concerning the quantities of salts of radium existing at the present time in the different scientific and medical laboratories of the globe, shows us that there are not more than six or seven grms. of metallic radium in the whole world. The industry of radium was born in 1899 from the impulse given to it by the studies of Pierre Curie. At a lecture given at the Society of Civil Engineers, M. Paul Besson has just now recalled the fact, that from that period till 1904, from 13 tons of pitchblende residuum, it was only possible to extract about 2 or 3 grms. of radium, which served specially to supply the laboratory of M. and Mdme. Curie. But an Austrian law put a stop to the exportation of the radio-active ores of Joachimstal. Radium was then extracted in France from much poorer ores containing only from a half to two mgrms. of radium per ton; such as the antimonites which come from Portugal or the carnotites from Colorado, whereas the residues of pitchblende contained from 100 to 200 mgrms. of radium per ton. During the last few years Austria has not treated more than 3 or 4 tons of pitchblende per year, from which were extracted annually less than 1 grm. of radium. America and England do not as yet produce radium salts. It is France which at present controls the production and the market of the precious metal. The price of a grm. of hydrated bromide of radium remains about 400,000 francs (£16,000) more or less, which means that a grm. of pure metallic radium is worth about 780,000 francs (£31,200). The principal possessors of radium are Mdme. Curie, whose laboratory contains from about 2·6 grms. to 3 grms. of radium, and Sir Ernest Cassel of London. As to the different applications of radium, they are well known. Besides its employment in medicine and therapeutics, its use in industry is spreading more and more. It has been possible to realise, with this metal, certain apparatus enabling the measurement of the potential of a conductor at a distance, without contact. Lastly, in silk factories, radium has been employed for de-electrifying not only the textile fibres but also parts of the machinery.

Gallium is Not Rare.

After a long series of researches, guided by the works of Mendeleeff, one of the rarest of metals, "gallium," in the blende of Pierrefitte, by the French chemist Lecoq de Boisbaudran, in 1875, has just been found in commercial aluminium. M. J. Bardel, director of one of the services of the Institute of Hydrology of the Collège de France, and M. C. Boulanger have made a spectrographic examination of ordinary aluminium, and in it they discovered the presence of "gallium." In a paper presented by Professor Haller, in their name, the two chemists indicate that, in treating 2 kilogrms. of aluminium, they have obtained nearly 4 decigrms. of gallium. Ordinary aluminium contains, then, nearly 0·02 per cent of this metal supposed to be so rare. It is a greater percentage than that attributed by Lecoq de Boisbandran to the blende of Pierrefitte.

Signs of Fatigue.

After having studied the conditions of very hard work with the physiological limits of fatigue, M. Jules Amar, in a new paper presented before the Academy of Sciences by Professor Dastre, has just examined what are the respiratory signs of fatigue. A double pneumograph, held in place during the whole duration of the experiment, has tracings of respiration that were easily compared. On the other hand, the gaseous outputs of the respiration were measured every two minutes. The alimentation of the persons under survey was the same for all: a simple cup of coffee well sugared, two hours before taking measurements. These conditions being established, M. Jules

Amar remarked that the frequency of the respiration increases with the work, but without any rigorous proportionality. It is, on an average, thirty-two respirations per minute, for the usual speed of a workman. With great speed fatigue is produced and puts an end to the work when it is hardly begun; that is to say, at the end of four minutes at the most. The frequency of the respiration is then somewhere about forty. Amplitude also increases with the work. The respirations are deeper and still deeper; they are barely more than twice as deep as when at rest. But if the work is continued till fatigue ensues, the amplitude of the respirations diminishes gradually and different irregularities are to be remarked. If the work is very hard, by an excess of effort or speed the respiratory output is irregular with accentuated ups and downs, but as a rule it goes on increasing until loss of breath occurs.

Election of Non-Resident of the Academy of Sciences—J. H. Fabre's Candidateship Withdrawn.

The fourth chair for a non-resident member of the Academy of Sciences—a section newly created by the decree of the 17th March, 1913, and reserved for provincial scholars—has been awarded to M. Charles Deperet, Dean of the Faculty of Science of Lyons, and to whom are due numerous and interesting geological works. His researches embrace the tertiary history of the Mediterranean basin. M. Deperet was elected with thirty-two votes, and the entomologist, J. H. Fabre, obtained two votes. We believe that at the secret committee meeting, held after the public sitting, the two eminent naturalists who had voted for the entomologist of Serignan, whose whole life has been consecrated to the study of the habit and lives of insects, have withdrawn his candidateship. In a written notice they said they said that J. H. Fabre had not stood for election, considering, on the other hand, from the votes of the commissions already elected, that he was not likely to succeed; the two savants not wishing to expose a man of M. Fabre's age to the humiliation of being refused, they simply withdrew his candidateship, which they themselves had proposed.

The High Atmosphere.

The results of the Franco-Swedish exploration of the high atmosphere during the three campaigns from 1907 to 1909, undertaken by Professor Hildebrandsson, of Upsala, and the late regretted Tesserenc du Bort, have just been published by M. Meurice, who took part in the expedition. M. Deslandres, Director of the Observatory of Meudon, recalls to mind that it is to Tesserenc du Bort that is due the discovery of the stratosphere, a layer of isothermal air whose temperature, extremely low, is constant through a great thickness. This layer, discovered for the first time at the Observatory of Trappes, at an altitude of from eight to ten kilometres, has again been found at the Equator at a still higher altitude, and its temperature there is somewhat lower. In the polar region, at Kiruna, situated at the north of the Scandinavian peninsula, Hildebrandsson and Tesserenc du Bort remarked the presence of the same isothermal layer. Numerous soundings with pilot balloons have allowed it to be proved that the temperature of the stratosphere was the same as that observed at Trappes. However, there is a difference between the temperatures of the lower layers of Lapland and of France. Nearly all the pilot balloons sent up by the two meteorologists have been recovered. M. Delandres has also announced that the Minister of War was about to accept the observatory of Trappes, which is offered to him by the Tesserenc du Bort family.

Physical Society's Annual Exhibition.—This Exhibition will be held on Tuesday, December 16th, at the Imperial College of Science, and will be open both in the afternoon and evening.

PROCEEDINGS OF SOCIETIES.

INSTITUTE OF CHEMISTRY.

At a Meeting of the Institute of Chemistry held at the Imperial College of Science and Technology, South Kensington, on Wednesday, October 29th, Prof. R. Meldola, LL.D., F.R.S., in the Chair, the first of two lectures was delivered by W. P. Dreaper, F.I.C., on "*The Research Chemist in the Works, with special reference to the Textile Industry.*"

The lecturer pointed out the difficulty in expressing opinions which could be universally accepted, for industrial chemists worked under such varying conditions and were influenced by temperament and past training. His remarks should therefore be taken as applying especially to the textile industry.

The total gross value of the Textile Industry (First Census of Production, 1907) indicated that the value of the textile materials and fabrics manufactured in the United Kingdom amounted to the total of £333,000,000; and that 1,253,000 persons were employed in their manipulation. Power to the amount of 1,900,000 h.p. was utilised, and 77 per cent of the firms used coal to the value of £8,137,000. On a basis of one chemist for every 2000 persons employed, no less than 600 chemists would be utilised in this industry alone; each of whom would deal with an annual gross output valued at over £500,000. A saving of 10 per cent in the coal bill would amount in all to £1,000,000. It would be remembered that one large aniline dye combine on the Continent already employed no less than 700 chemists. The recently made statement that "Science was fast becoming an industry" seemed to apply in this case at any rate.

Stress was laid upon the value of a satisfactory knowledge of the principles underlying analysis to the student entering a works. He must expect to work on the borderland of industrial research, and therefore to devise new methods of a chemical or physical nature to record his progress. Actual examples were given of the difficulties met with in interpreting the figures obtained. The results that the successful investigator might achieve by working out new methods and processes, or improving those already employed in works, were indicated, and the advantages of secret working were also dealt with. Also the effect produced through the stress of competition and the utilisation of new processes on working conditions. It was urged that the chemist should spend as much of his time as possible in the works, entering the laboratory when systematic investigation was necessary. The industrial chemist who remained in his laboratory was lost. Knowledge of chemistry alone was an insufficient equipment, modern research being set on a wide basis, and requiring a knowledge of physics and the power to apply this in many directions. This was demonstrated at every turn.

After describing a typical college dyeing department, the fitting up of a works research laboratory was briefly considered. It was pointed out that experiments utilising more than 5 to 10 h.p. should be conducted in the works itself. The fitting up of experimental works as a preliminary to establishing an industry was discussed. Such a station had been known to utilise 10,000 h.p. for experimental purposes.

The work of the textile chemist was then considered in greater detail, and specially illustrated by reference to the early developments in Mercerising and Schreinering. Both these processes were shown to depend upon certain details, which although actually patented in the former case were not fully realised in the early experiments. The chemist working under industrial conditions would at once realise the success achieved by the rule-of-thumb man in the past; by systematically studying his methods, and seeking to discover points he had not fully realised, the chemist may often be able to improve upon them. Workmen who control operations of vital importance should be "discovered"

by the chemist; their methods studied in the light of his more specialised knowledge. Important results could often be secured by inquiring into the origin of so-called defects in manufacture.

The nature of the methods and machinery used for producing artificial fibres, and more recently artificial fabrics, was then indicated; samples being exhibited of many of the different products already obtained. The part to be played by the chemist was pointed out, as well as the great need for further research in this direction.

The remaining portion of the lecture dealt with the influence of theory and the chemist's work on actual industrial operations, and concluded with a brief discussion on the modern theories in connection with dyeing and investigations which have had their origin in observations originally made in the dye-house.

NOTICES OF BOOKS.

The Volatile Oils. By E. GILDEMEISTER and FR. HOFFMANN. Second Edition by E. GILDEMEISTER. Translated by EDWARD KREMERS. Volume I. London, Bombay, and Calcutta: Longmans, Green, and Co. 1913.

THE second German edition of this treatise has been expanded into two volumes, the first of which deals with the history of the several volatile oils, and also contains descriptions of the chief constituents of the oils and of methods of examining and test ng them and detecting adulterants. The history of methods of distillation from those employed in primitive times down to the most modern processes is fully treated, this part of the book having been written by the late Dr. Friedrich Hoffmann, and only very slightly altered in the new edition. A new chapter has been added on the production of flower perfumes by extraction, enfleurage, and maceration, while the chapter on the theory of the separation of the ethereal oils by distillation has been omitted. The translator has thought it advisable to condense some chapters to a certain extent, but, on the other hand, he has added details of a few oils to the special part, and has included some new results which have been published quite recently.

Production et Consommation des Engrais Chimiques dans le Monde. ("The World's Production and Consumption of Chemical Manures.") Rome: Institut International d'Agriculture. 1913. (3 francs.)

THIS monograph has been prepared for the Committee of the Italian Bureau of Agricultural Intelligence and Plant Diseases, by Dr. G. A. R. Borghesani, who has taken the utmost trouble to collect all the latest reliable data and arrange them in the most accessible and convenient form. He addressed a circular letter to the Governments of practically all the countries of the world asking for information as to the production and consumption of manures, and from their replies, which were in most cases very detailed, he compiled the statistical tables which occupy a large part of the monograph. He also visited many European countries for the purpose of getting a first-hand knowledge of many details. Although necessarily far from complete the monograph will provide a valuable foundation for future work on the subject; it is intended to issue half-yearly summaries of the production and consumption of fertilisers, and thus keep the information quite up to date.

Canadium, the Supposed New Element.—In the Annual Report of the British Columbia Minister of Mines it is stated that authentic samples of the dyke in which the presence of platinum metals and "canadium" had been reported, were procured and submitted, together with concentrates from the crushed material, to representa tive firms of assayers, to the Canadian Geological Survey, and to the British Columbia Government Laboratory. In no case were any traces of platinum metals detected, nor was there any evidence of the presence of the alleged new metal.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Academie des Sciences. Vol. clvii., No. 9, September 1, 1913.

This number contains no chemical matter.

Vol. clvii., No. 10, September 8, 1913.

Experiments on the Cupric Hydrates and the Heat of Formation of Copper Nitrate.—M. de Forcrand.—Péligot's hydrate of cupric oxide, $CuO.H_2O$, does not lose weight even when kept over sulphuric or phosphoric acid at 30°. When heated to 85° it changes colour, becoming green, but does not lose weight. If heating is continued it begins to undergo hydration; thus at 100° it becomes olive green, and its formula corresponds to $CuO+0.8H_2O$. It then turns brown, and is converted into the hydrate $CuO+0.35H_2O$. By determining the heat of solution of these different hydrates in dilute nitric acid it is found that the isomeric change of the blue into the green hydrate is exothermic and corresponds to 0·261 cal. The heat of formation of anhydrous copper nitrate is 71·49 cal., and for a solution 81·96 cal. These values approximate closely to those obtained for uranyl nitrate, and the mean for the two metals is the same.

Mechanism of the Formation of Sulphuric Acid in the Lead Chambers.—E. Briner and A. Kuhne.—When sulphuric acid is produced in the lead chambers the atomic oxygen set free by the dissociation of NO_2 into NO and O plays an important part; the atoms of oxygen combine with SO_2 far more readily than molecules, and they are continually regenerated by the dissociation of NO_2. The anhydride SO_3 readily gives H_2SO_4 with water, and in consequence of its low vapour tension at the temperature of the chambers (40—60°) it rapidly condenses.

MEETINGS FOR THE WEEK.

TUESDAY, 11th.—Chadwick Public Lectures, 5. (The University of London, South Kensington). "The Place of the Open-air School in Preventive Medicine," by Sir George Newman, M.D.

WEDNESDAY, 12th.—Biochemical Society, 5.30. (In the Physiological Laboratory, King's College, London).

THURSDAY, 13th.—Royal Society. "The Preparation of Eye-preserving Glass for Spectacles," by Sir William Crookes. "On An Inversion-point for Liquid Carbon Dioxide in regard to the Joule-Thomson Effect," by A W. Porter. "Negative After-images and successive Contrast with Pure Spectral Colours," by A. W. Porter and F. W. Edridge-Green. "The Positive Ions from Hot Metals," by O. W. Richardson. "Diurnal Variation of Terrestrial Magnetism" and "A Suggestion as to the Origin of Black Body Radiation," by G. W. Walker.

FRIDAY, 14th.—Physical, 8. "Thermal Conductivity of Mercury by the Impressed Velocity Method," by H. R. Nettleton. "Polarisation and Energy Losses in Dielectrics," by A. W. Ashton. A Lecture Experiment to illustrate Ionisation by Collision and to show Thermo-luminescence, by F. J. Harlow.

— Alchemical Society, 8.15. (At International Club, Regent Street). "The Hermetic Mystery," by Mdme. Isabelle de Steiger.

THE CHEMICAL NEWS.

Vol. CVIII., No. 2816.

THE CONSTITUTION AND STRUCTURE OF THE CHEMICAL ELEMENTS.

By HAWKSWORTH COLLINS.

There are two methods employed by scientists of discovering scientific truths:—

(a) Discovery by direct experiment; *e.g.*, the fact that radium splits up into helium and niton.
(b) Discovery by reasoning upon several allied experimental facts; *e.g.*, the discovery of Newton's First Law of Motion.

The former method, which of course must precede the latter, only discovers isolated truths, and does so in new directions generally by accident; *e.g.*, the discovery of the fact that helium and oxygen can combine to form neon was accidental. The latter method, if correctly done, has a great advantage over the other, for it must of necessity show the way to further discoveries since it demonstrates the reason of things. The results of reasoning are sometimes for ever incapable of proof by direct experiment; *e.g.*, Newton's First Law of Motion. Some results of reasoning may be incapable of direct experimental proof under our present knowledge, although the conditions may be altered by the advancement of knowledge. An example of this is afforded by the present condition of the facts which demonstrate the constitution and structure of atoms. The elucidation of this statement will appear in the following matter.

The following discoveries have been made in duplicate by the two methods within the last ten years:—

In an α-ray change, when a helium atom carrying two atomic charges of positive electricity is expelled, the element changes its place in the Periodic Table in the direction of diminishing mass and diminishing group number by two places.—Prof. F. Soddy, 1911.	The non-metallic nature of an element is always due to a pair or pairs of electropositive forces, each pair emanating from a portion of the element, of which the mass is 4, taking the mass of an atom of hydrogen as unity.—Advt. in *Nature*, June 14, 1906, asking for expert opinions.

If there is any difference between these two statements it would be interesting to know what the difference is, for the latter statement is exactly the same as the following:—"If a helium atom (at. wt. 4) carrying two charges of positive electricity could be expelled from several of the simple elements, the residual product would be two places lower in the Periodic Table, since the element would have lost two valencies together with a mass of 4."

The statement on the left was obtained by direct experiment from the *radio-active* elements; that on the right from reasoning upon facts with regard to the *simple* elements.

An element, whose atomic weight is 3, is the only element of low atomic weight which has been discovered within the last ten years. It is found by Sir J. J. Thomson to be given off by all kinds of substances, a fact which leads him to think sometimes that the elements of low atomic weight are splitting up.	H_3 is the only new element, which was discovered ten years ago by reasoning to be a necessary part in the constitution and structure of nearly all the simple elements, and it was printed in the Chemical News of March 24, 1910 (vol. ci., p. ii.) as an element, and called H_3 (Asterium).
Messrs. Collie and Patterson discovered this year (1913) that helium and oxygen can combine to form neon.	In the Chemical News of March 24, 1910 (vol. ci., p. ii.) the structure of neon was given as the combination of the structures of helium and oxygen.

It is absolutely impossible for any one to integrate facts to such a degree of detail so as to be in accordance with the latest discoveries of modern science, and yet not to have obtained the truth.

It follows from this that the first main principle in the constitution and structure of all the chemical elements, whether radio-active or otherwise, has been *proved;* and it is this:—"In a large number of the elements two electropositive valencies emanate from a portion of the element of which the mass is 4."

If the body of atomic weight 3 observed by Sir J. J. Thomson is not a product of the disintegration of some of the simpler elements, and if it is simply absorbed in some manner by nearly all kinds of substances, then all the *exact* determinations of the atomic weights of the elements are completely upset, and it is quite absurd for scientists to say that it has been proved, for instance, that the atomic weights of elements are not all whole numbers.

The presence of this terribly large source of error must be worrying the International Committee on Atomic Weights, since it seems to be necessary for scientists to expel all traces of it and start the determination of the atomic weights all over again.

But, since the atomic weights of several of the common and important elements, *e.g.*, B, C, F, O, and Na, are now given as exactly whole numbers, it is evident that this source of error cannot have affected them, for it is quite impossible for scientists to arrive at these beautiful results and yet not to have obtained the truth. Therefore, Sir J. J. Thomson's X_3 is not an impurity but is a product of the disintegration of the simpler elements.

Prof. F. Soddy said in the Chemical News in the early part of this year (cvii., 97), that all attempts to find numerical relations between the atomic weights of the elements had ended in failure. It is evident, therefore, that the most obvious relationship which was ever discovered has been stowed away, forgotten, and ignored by scientists. It was published by the Chemical News, in a paper, not as an advertisement. (Results put in as advertisements by the author are those which are likely to be outrageous to scientists of the time).

The discovery was as follows:—"Considering only elements of atomic weight less than 60 (because the possible errors in numerical data for elements of low atomic weight are less than for those of high atomic weight), *whenever the atomic weight of an element approximates to, or is nearer to, an even whole number, its valency is even, and when it approximates to, or is nearer to, an odd whole number, its valency is odd*, with the possible exception of nitrogen."

This fact, taken in conjunction with the fact that an error in the determination of atomic weights must have arisen from the observance that protyle, which is something like the thousandth or two-thousandth part of the mass of an atom of hydrogen, can be expelled from nearly all substances, and also taking into consideration the fact that the atomic weights of the elements are evidently hovering round whole numbers, *proves that the atomic weights of the elements are whole numbers.* For, if not, what do they mean by hovering round whole numbers, and why are 7 out of 28 given as exactly whole numbers, and why are 21 out of 28 not more than 0·1 from whole numbers?

The facts with regard to this matter are now placed in tabular form. (See accompanying Table).

In *Nature*, December 26, 1901, it is asserted that glucinum is probably a triad, but the Periodic Law stands in the way. The "Periodic Law" has no business to stand in the way, for it is not a law, but only an ex-

Element.	Atomic weight (1913).	Difference from whole numbers.	Nearest whole number.	Remark.	Maximum valencies.	Remark.
Hydrogen	1·008	0·008	1	Odd	1	Odd
Helium	3·99	0·01	4	Even	2	Even
Lithium	6·94	0·06	7	Odd	1	Odd
Glucinum	9·1	0·1	9	Odd	3	Odd
Boron	11·0	0·0	11	Odd	3	Odd
Carbon	12·0	0·0	12	Even	4	Even
Nitrogen	14·01	0·01	14	Even	6 (?) (NO_3)	Even
Oxygen	16·0	0·0	16	Even	2	Even
Fluorine	19·0	0·0	19	Odd	1	Odd
Neon	20·2	0·2	20	Even	0	Even
Sodium	23·0	0·0	23	Odd	1	Odd
Magnesium	24·32	0·32	24	Even	2	Even
Aluminium	27·1	0·1	27	Odd	3	Odd
Silicon	28·3	0·3	28	Even	4	Even
Phosphorus	31·04	0·04	31	Odd	5	Odd
Sulphur	32·07	0·07	32	Even	6	Even
Chlorine	35·46	0·46	35	Odd	7	Odd
Potassium	39·10	0·1	39	Odd	1	Odd
Calcium	40·07	0·07	40	Even	2	Even
Argon	39·88	0·12	40	Even	0	Even
Scandium	44·1	0·1	44	Even	4 (ScO_2)	Even
Titanium	48·1	0·1	48	Even	4	Even
Vanadium	51·0	0·0	51	Odd	5	Odd
Chromium	52·0	0·0	52	Even	6	Even
Manganese	54·93	0·07	55	Odd	7	Odd
Iron	55·84	0·16	56	Even	4 or 6 (ferrates)	Even
Cobalt	58·97	0·03	59	Odd	3	Odd
Nickel	58·68	0·32	59	Odd	3 (Ni_2O_3)	Odd

ceedingly useful observation. Who ever heard of a law which makes an indefinite statement? It asserts that "the properties of elements are periodic functions of their atomic weights." What functions? Nobody has yet been able to discover. It follows from this law that specific gravity (*e.g.*) is *a* periodic function of atomic weight. The word "a" here is the *indefinite* article, and has no business to appear in the statement of a *law*. It denotes uncertainty. In Newton's First Law of Motion the word "a" occurs, but there is no uncertainty in it. The law is as follows:—Every body remains in its state of rest or of uniform motion in *a* straight line, unless it is compelled by some external force to alter that state.

The remark, which is continually occurring in scientific papers, that the Periodic Law requires amendment, is evidently fully justified.

The Periodic observation is now out of date, for it was merely an observation, the reason for it being then unknown; but the reason is now known, and therefore must take the place of the observation.

The mathematical probability that the two columns of remarks on even and odd whole numbers would exactly correspond *by accident* is $1:2^{28}$, *i.e.*, 1:268,435,456.

The probability that they would accidentally correspond with only one exception is $1:2^{26}$, *i.e.*, 1:67,108,864; with only two exceptions, $1:2^{24}$, *i.e.*, 1:16,777,216; with three exceptions, 1:4,194,304; with four exceptions, 1:1,048,576.

If any one thinks that there are as many as four exceptions, even then it has been proved that the probability is at least one million to one that the correspondence is not the result of an accident, and the general rule holds that if the atomic weight of an element approximates to an even whole number its maximum valency is even, and if the atomic weight approximates to an odd whole number, its maximum valency is odd.

This general rule, taken in conjunction with all available facts, leads to the deduction published (as stated) in *Nature* on June 14, 1906.

Supposing that it is admitted that nitrogen is certainly an exception to the general rule, although the molecule NO_3 has been recorded, many scientists would say that this exception upsets the rule; but it does not do anything of the kind—it proves the rule.

If any one thinks that an exception does not prove the rule, he is asked to consider the following statement:—"The solar system is composed of an approximately spherical body, called the Sun, round which revolve approximately spherical bodies, called Planets, around which revolve approximately spherical bodies, called Satellites." This is the general rule. But the fact that Saturn is accompanied by rings as well as satellites, does not upset the general rule. It only emphasises it, and leads to something deeper; for the rings of Saturn may be in the process of disclosing to us the method by which satellites are produced.

If, after what has been said, scientists are prepared to consider the second main principle in the constitution and structure of atoms, which is a more general observation than the first, it is ready to be produced; but, if not, it will have to wait for a more convenient season. It would not do scientists much harm to condescend to look at it. It might do a little good in showing the way to further successful experiments.

RECENT WORK IN INORGANIC CHEMISTRY.*

By JAMES LEWIS HOWE.

(Continued from p. 229).

Group III.—There have been many attempts to isolate hydrogen boride, which is formed when magnesium boride is acted on by acids and which colours the flame of the simultaneously evolved hydrogen green, and which is also recognisable by its bad odour. The amount of hydrogen boride present is exceedingly small and it is so unstable that until very recently all efforts to isolate it for analysis have been futile, although Ramsay and Hatfield considered it probable that the formula of the gas they obtained was H_3B_3. Stock and Massenez (*Ber.*, xlv., 3539) have now in part solved the problem and their results are a surprise, for the simplest gas evolved in the above reaction is $H_{10}B_4$, and this is accompanied by another whose formula is probably $H_{12}B_6$, as well as others, apparently formed by

* *Journal of the American Chemical Society*, xxxv., No. 2.

the decomposition of the latter, which were present in too small quantity to be studied. The difficulties of previous experimenters has arisen from the small quantities of the borides formed, their great instability, especially in the presence of water, the difficulty of separating the different borides formed in the reaction, and the unavoidable presence of at least the hydrogen silicides, from the silicides in the magnesium boride used. The hydrogen borides were prepared by letting the finely powdered magnesium boride fall slowly into acid, and condensing by liquid air, the total yield being under most favourable circumstances 1·2 cc. per litre of evolved hydrogen. The liquid obtained was fractioned, and after great difficulties sufficient of the above compounds obtained for study. $H_{10}B_4$ boils at 16° and $H_{12}B_6$ at a higher temperature, probably near 100°. Both ignite in contact with the air, and decompose in water, giving compounds similar or identical with those described by Travers and Ray. These chemists (*Proc. Roy. Soc. London*, (A) lxxxvii., 163), by fusing a mixture of magnesium powder with B_2O_3 in hydrogen, obtained a grey powder which, when treated with water, slowly evolved a gas. The solution became yellow and was slightly alkaline. On boiling this solution hydrogen is given off and when treated with acid still more copiously. The gas has a peculiar odour and burns with a green flame, but analysis shows it to be nearly pure hydrogen. It apparently contained traces of a boron hydride (as Stock has found). On distilling the solution a compound passes over which has the formula B_2O_3, but which is not boric anhydride, though evidently an isomer of it. The authors consider that the original powder contains not only Mg_3B_2 but also Mg_2B_4; that from these are formed by the action of water B_4O_2 and B_4O_3, which are further acted on by the water with the formation of the oxide B_2O_3 above mentioned and "boron hydrates" (a name not well chosen) of the respective formulæ $B_2O_2H_6$ and $B_2O_3H_6$.

In the continuation of his work on Scandium, Meyer (*Nernst-Festschrift*, cccii.; Chem. News, cvi., 13) calls attention to the fact that unless a very large excess of KIO_3 is used in separating thorium from scandium, a small amount of thoria remains dissolved in the solution of scandium iodate. This scandium, and also scandium separated by the sodium carbonate method, showed no radioactivity and was spectroscopically pure, yet had an atomic weight of 45. Further purification with KIO_3, with great sacrifice of scandium, brought the atomic weight down to 44, and thorium could be identified in the portion precipitated. It is thus possible for scandia to contain upwards of 0·5 per cent thoria which cannot be detected directly by chemical or physical means. However, Meyer shows that the magnetic method of detection is available, since the product with atomic weight of 45 is paramagnetic, while the pure product (44) is diamagnetic. He calls attention to the fact that scandium, lanthanum, and yttrium, which unquestionably belong to the third group of the periodic system, are distinguished by their magnetic character from all the other rare earths. Among the other works which have appeared on the rare earths are those of James (*Journ. Am. Chem. Soc.*, xxxiv., 757) on their separation; of Jantsch (*Zeit. Anorg. Chem.*, lxxvi., 303) on the double nitrates; of Wirth (*Ibid.*, 174) on the solubility of the oxalates and sulphates in sulphuric acid; and of Barnebey (*Journ. Am. Chem. Soc.*, xxxiv., 1174) on the reactions of the rare earths in non-aqueous solutions. Urbain and Bourion (*Compt. Rend.*, cliii., 1155) have also prepared and studied the chlorides of europium, $EuCl_3$, $EuCl_2$, and EuOCl. These papers are all valuable contributions to this interesting subject, but do not lend themselves to brief abstraction.

Group IV.—The question as to what is the first reaction that takes place when carbon burns in oxygen has long been a subject of controversy. The commonly accepted view that the initial combustion is to CO_2, which in the presence of incandescent carbon is reduced to CO, rests experimentally chiefly on the work of Lang, who found that in a slow oxygen stream carbon was oxidised at 500° almost exclusively to CO_2, while no CO_2 was reduced to CO at this temperature. The formation of *some* CO in a more rapid gas current Lang attributed to local heating, which did not occur in the slow current. The conclusions drawn from these and other experiments by Lang were called in question by Dixon, and his experiments and those of Baker on explosion of rates seemed to show that at least in the case of gaseous carbon the formation of CO precedes that of CO_2. C. J. Baker also showed that while moist oxygen absorbed by carbon at −12° was given up as CO_2 when the carbon was heated to 100°, dry oxygen (by P_2O_5) absorbed by dry carbon at +12° was not given up till 450° and then mainly as CO, it appearing thus that CO is the first product of oxidation. Rhead and Wheeler (*Journ. Chem. Soc.*, ci., 831, 846) have approached the subject from the standpoint of determining the velocity of the reaction (*a*) $C+O_2=CO_2$; (*b*) $CO_2+C=2CO$; (*c*) $2C+O_2=2CO$; and (*d*) $2CO+O_2=2CO_2$, at different temperatures. If it could be shown that either reaction (*a*) or reaction (*c*) proceeded at a temperature at which, under the same experimental conditions, the rates of reactions (*b*) and (*d*) were inappreciable, the problem would be solved. It was, however, not found possible to obtain a temperature at which the velocity of carbon oxidation was appreciable, where there was conclusive evidence of the primary formation of either oxide to the exclusion of the other. Some CO is produced by the oxidation of carbon at low temperatures under conditions which do not admit of its being formed by the reduction of CO_2, but on the other hand CO_2 is undoubtedly produced at low temperatures in quantity which cannot be altogether accounted for by the supposition that CO is first formed and then oxidised to CO_2. The conclusion is therefore drawn that when carbon is burned at low temperatures CO_2 and CO are produced simultaneously, a conclusion quite in accord with practically all previous experimental evidence. A further paper is promised on what reaction between carbon and oxygen can account for this simultaneous production of two oxides. The question as to whether carbon monoxide burns directly to the dioxide $2CO+O_2=2CO_2$, has in the past stimulated much investigation, especially since it seems certain that the reaction does not go on, even at high temperatures, unless at least a trace of water is present. Now Wieland (*Ber.*, xlv., 679) has shown that carbon monoxide is oxidised by moist palladium black, even in the absence of oxygen. It appears that the first step of the reaction is the union of CO and H_2O to formic acid, and that this is in turn decomposed to CO_2 and hydrogen, the latter being absorbed by the palladium black. If the same reaction goes on in the ordinary combustion of carbon monoxide, then the hydrogen evolved is at once oxidised to water and the cycle repeated. Wieland was able to show the formation of formic acid in the combustion of carbon monoxide by directing the flame against ice, when formic acid was detected in the water.

An examination of the air collected on the Charcot Antarctic expedition has been made by Müntz and Lainé (*Compt. Rend.*, cliii., 1116) and the amount of CO_2 found to vary from 1·447 to 2·553 parts per 10,000, the mean being 2·0524. The small amount compared with the normal content is to be accounted for by the temperature of the ocean water, generally below 0°, thus reducing the dissociation pressure of the dissolved bicarbonates. This is in confirmation of the theories of Schloesing, and shows that, contrary to the idea of Gay-Lussac, the movement of the atmosphere is not sufficient to cause a uniform distribution of CO_2. It is to be hoped that there will soon be opportunity for a study of the atmosphere over the Antarctic plateau, where the influence of the ocean would be eliminated. The composition of the higher layers of the atmosphere is considered by Wegener (*Zeit. Anorg. Chem.*, lxxv., 107) to be very different from that of the lower strata. His views are based on the changes of density as shown by the suspension of the Krakatoa dust

clouds, diffuse reflection of light, and also of sound, the glow of meteors and spectra of the aurora and of meteor trails, and also the analogy of the sun's atmosphere. At 40 kilometres oxygen is reduced one-half and nitrogen correspondingly increased. Above this these gases rapidly decrease, while hydrogen increases and helium is at a maximum of 4 per cent. At 200 kilometres and above, the chief constituent is a gas lighter than hydrogen, called by Wegener geo-coronium, resembling the coronium of the sun, and possibly identical with Mendeleeff's element with atomic weight of 0·4.

A further substantiation of the theories of Franklin on ammono-compounds, fully recapitulated by him and also applied to the mercury-ammonia compounds (*Am. Chem. Journ.*, xlvii., 285, 361), is furnished by the work of Ruff (*Ber.*, xlv., 1364) on the nitrogen compounds of quadrivalent titanium. The starting-point was $TiBr_4$, formed by the action of bromine in a stream of carbon dioxide on metallic titanium or its carbide. On treatment with ammonia this gives an ammonate of approximately the composition $TiBr_4.8NH_3$. By washing with liquid ammonia this is more or less ammonolysed, giving a product (ammono-basic bromide) containing both titanium amide, $Ti(NH_2)_4$, and bromide, of somewhat variable composition. From this, by action of potassamide, KNH_2, there was formed a new titanium nitride, Ti_3N_4, and a potassium ammono titanate of the formula $KHTiN_2$ (structurally, $\begin{matrix}KN\\HN\end{matrix}\!\!\geqq Ti$). The nitride, Ti_3N_4, is hydrolysed by water with the formation of titanic acid and ammonia, and on heating is converted into the nitride of trivalent titanium, TiN, and nitrogen. The possibility of utilising this reaction for the synthesis of ammonia from its elements is suggested by the author, and an experiment of heating a mixture of hydrogen and nitrogen to 360° in the presence of the above-mentioned potassium salt showed a contraction of volume, which indicated ammonia formation. The potassium ammono-titanate ignites spontaneously in the air and is violently decomposed by water. A portion of the potassium (3/10) can be removed by washing sufficiently with liquid ammonia. With potassium iodide or sulphide the potassium seems to be replaced by iodine or sulphur, indicating, as would be expected, the amphoteric nature of the TiN_2 group.

Group V.—A rather extensive piece of work has been carried out by Ferratini (*Gazz. Chim. Ital.*, xlii. [1], 138) on the double salts of hydrazine. These were generally prepared by mixing solutions of the components, if soluble, but occasionally by solution of the oxide or halide in an acid solution of the hydrazine salt. In many cases, especially with bivalent metals, the salts were hydrated, and in a few cases contained "hydrazine of crystallisation" (hydrazinates). No systematisation of the types appears possible. For example, Cu^{I} gives $3CuCl.N_2H_5Cl$, $CuCl.N_2H_5Cl$, $CuCl.N_2H_5Cl.0{\cdot}5H_2O$, $3CuBr.2N_2H_5Br$, $2CuCN.N_2H_5CN$; Sb and Bi give the $SbCl_3.3N_2H_5Cl$ type, but Fe'' and Mn'' give the same, as $FeCl_2.3N_2H_5Cl$; while Co and Ni give $CoCl_2.2N_2H_5Cl.2{\cdot}5H_2O$ and $CoCl_2.2N_2H_5Cl.0{\cdot}5N_2H_4$. Zn gives $ZnI_2.2N_2H_4I.0{\cdot}5H_2O$, while the similar salt of Cd is anhydrous. In many respects these salts naturally show much analogy with the corresponding NH_4 salts. An interesting derivative of hydrazoic acid with cyanogen has been prepared by Darzens (*Compt. Rend.*, cliv., 1232). By the action of NaN_3 upon cyanogen bromide, $N{\equiv}C.N_3$ is formed, called by Darzens carbon pernitride, but better cyanogen trinitride (or hydrazoate). CN_4 is a colourless oil which crystallises in needles melting at 36°, and is soluble in most organic solvents. Slightly volatile in a vacuum, it begins to decompose at 70° and explodes at 170° with great violence. It is exceedingly sensitive to shock, but in a perfectly pure condition can be preserved a long time. It readily undergoes polymerisation, forming a solid which is insoluble in ether and not exploded by a blow. The aqueous solution of CN_4 readily hydrolyses to the acid, $N_3.COOH$, which in turn decomposes into HN_3 and CO_2.

Three papers have appeared from Ephraim (*Ber.*, xliv., 3405, 3414, 3416) on substituted phosphoric acids. Owing to hydrolysis the only tetrathiophosphate hitherto prepared is that of sodium. It is possible that the anion of this salt, $PS_4{}^{---}$, hydrolyses, but more probable that it must be considered as decomposing, $2Na_3PS_4 \rightleftharpoons 2Na_2S+P_2S_5$, the P_2S_5 then hydrolysing. Antagonising this reaction by the use of a large excess of alkaline sulphide with a minimum of water, Ephraim was able to prepare from P_2S_5 the tetrathiophosphates of potassium, ammonium, and barium, but with strontium only a hydrogen trithio-salt, $Sr_3H_6(PS_3O)_4.aq.$ Ephraim protests against these compounds being called *sulpho* phosphates, since a *sulpho*-compound should be derived from SO_3H. They should be called thiophosphates, *thio* being used for those compounds in which *bivalent* sulphur replaces oxygen. For the different acids of this series he proposes the names: for $(HO)_3P:S$, *thion*-phosphoric acid; for $\begin{matrix}(HO)_2\\HS\end{matrix}P:O$, *thiol*-phosphoric acid; for $\begin{matrix}HO\\(HS)_2\end{matrix}P:O$, *dithiol*-phosphoric acid; and for $\begin{matrix}(HO)_2\\HS\end{matrix}P:S$, *thion-thiol*-phosphoric acid. When the lower oxides, P_4S_3 and P_4S_7, react with sodium sulphide, the same product seems to be formed, though with differing amounts of water of crystallisation. The formula corresponds to $Na_3PS_3.aq.$, but the compounds are not thiophosphates, since after removal of the sulphur by water a compound is left which reduced permanganate. In spite of the fact that the acid is tribasic (trithiophosphorous acid should be dibasic), Ephraim is inclined to think the compound is sodium trithiophosphite. When P_4S_7 is used in its preparation there is an evolution of spontaneously combustible phosphine, but with P_4S_3 only ordinary phosphine and hydrogen. By the treatment of the compound $P\begin{matrix}-OC_6H_5\\=Cl_2\end{matrix}$ with sulphur there is formed $S:P\begin{matrix}-OC_6H_5\\=Cl_2\end{matrix}$, and this with ammonia gives a beautifully crystallised and stable phenyl ester of diamino-thion-phosphoric acid, $S:P\begin{matrix}-OC_6H_5\\=(NH_2)_2\end{matrix}$. The free acid can be obtained from this by saponification with solid KOH and acidification, but not in a pure condition. The chloride of the diphenylester of phosphoric acid, $O:P\begin{matrix}=(OC_6H_5)_2\\-Cl\end{matrix}$ gives with hydrazine the ester of hydrazino-phosphoric acid, from which salts of this acid, $O:P\begin{matrix}=(OH)_2\\-NH.NH_2\end{matrix}$, can be prepared, as well as those from the monophenyl ester. The free acid is unstable but can be kept in alkaline solution. More than ten different salts of these two acids are described.

Group VI.—A number of studies of peroxy-salts have appeared during the year, among them two by Riesenfeld and Rau on the percarbonates (*Ber.*, xliv., 3589, 3595), who recognise three types of these compounds, the carbonate with H_2O_2 of crystallisation, the true percarbonates Na_2CO_4, and those of the $Na_2C_2O_6$ type. The compounds $Na_2CO_3.H_2O_2.0{\cdot}5H_2O$ and $Na_2CO_4.1{\cdot}5H_2O$ (types 1 and 2) are isomeric, but show even in solution different chemical characteristics. D'Ans and Frederich (*Zeit. Anorg. Chem.*, lxxiii., 325) have used as a method of preparing peroxides of alkalis and alkaline earths the solution of the metal in an ethereal solution of H_2O_2.

Quite an extensive study of aminosulphonic acid and its derivatives has been made by Hofmann (*Ber.*, xlv., 1394, 1731). The use of the acid, which crystallises pure and anhydrous, out of a not too concentrated solution of hydroxylamine hydrochloride which has been saturated with sulphur dioxide, is suggested as a standard for acidimetry. The acid is not hygroscopic and can be

accurately weighed. It can be titrated in 0·1 N strength against 0·1 N KOH with phenolphthalein or methyl orange, against 0·1 NH_3 with rosolic acid, and against 0·01 BaOH with phenolphthalein. In all these cases it gives accurate acid values. The 0·1 N solution is hydrolysed by 90 minutes boiling to the extent of 38·5 per cent, and 88 per cent in 11 hours. At 40° the hydrolysis is very slow, and at 15° not recognisable at the end of a week. Since the hydrolysis gives rise to ammonium hydrogen sulphate it does not affect the acid value, but owing to the presence of ammonium cannot be used with phenolphthalein as an indicator. Aminosulphonic acid is an excellent reagent for the preparation of aryl-sulphuric acids and phenol-sulphonic acids. An interesting series of salts is described in which the hydrogen of the NH_2 group is more or less replaced by Hg, Ag, or Au, as for example, $Hg:N.SO_2OK$, $AgHN.SO_2OK$, and $Au_2(N.SO_2OK)_3$.

The work of Gutbier on chloro- and bromo-tellurates has been continued (*Journ. Prakt. Chem.*, [2] lxxxvi., 150) by the preparation of a large number of these salts of organic bases, chiefly belonging to the aromatic series. The chlorotellurates are all yellow and the bromotellurates red. All are anhydrous and not one crystallises in the regular system. To these must be added (*Ibid.*, lxxxv., 321) a large number of bromo-selenates, both of the alkali metals, which are all octahedral, and of alkylammoniums. Hexabromoselenic acid, H_2SeBr_6, was prepared by acting on finely divided selenium in concentrated hydrobromic acid with bromine. On adding the bromide of the base, the anhydrous bromoselenates crystallise out. They are all easily hydrolysed, and the organic salts do not crystallise in octahedral form.

Group VII.—Salvadori (*Gazz. Chim. Ital.*, xlii., [1] 458) has investigated the hydrates and ammoniates of the perchlorates of the bivalent metals. The typical hydrate, as would be expected, is $M''(ClO_4)_2.6H_2O$, where M'' is Co, Ni, Mn, Cd, Zn, or Cu. A tetrahydrate is also formed in each case except that of Co, and with Cu the tetrahydrate is the stable form. Hexa-ammoniates, $M''(ClO_4)_2.6NH_3$, are formed with Co, Ni, and Cd, and tetra-ammoniates with Co, Cd, Zn, and Cu. Mn and Cu, while not giving hexa-ammoniates, form mixed compounds of the hexa-type, $Mn(ClO_4)_2.5NH_3.H_2O$ and $Cu(ClO_4)_2.4NH_3.2H_2O$. Cu has also a strong tendency to form basic perchlorates. An interesting case is that of five cobalt perchlorates, with respectively $6NH_3$, $4NH_3$, $3NH_3$, $4NH_3.2H_2O$, and $3NH_3.3H_2O$, which readily pass from one into the other on increasing or decreasing the vapour pressure of water and ammonia surrounding them. These are all strongly coloured, red, blue, or green, but another cobalt perchlorate exists, $Co(ClO_4)_2.2NH_3.2H_2O$, which is yellow, more stable than the others, and seemingly of an entirely different character. Another attempt has been made to prepare perbromic acid and the perbromates (Robertson, CHEM. NEWS, cvi., 50) and again unsuccessfully. Even up to 250°, bromine in the presence of KBr had no effect upon $KClO_4$, nor was the slightest trace of iodine given off from KIO_4 by the action of bromine. On heating $KBrO_3$ with PbO_2 the only product of the reaction was KBr. Robertson considers that in the formation of perbromic acid the vibration of the atoms within the molecule may be too great for such a system to exist. On the other hand, since both perchlorates and periodates are stable, it seems more probable that chemists have merely failed thus far to catch just the conditions demanded for the formation of the perbromates, as they have failed also to get the oxides of bromine.

Group VIII.—The colours formed by heating cobalt nitrate with various oxides, as in qualitative analysis, furnishes a perennial subject of research. Hedvall (*Ber.*, xlv., 2095) has prepared Rinmann's green in hexagonal crystals of some size (2—3 mm.²), by heating zinc oxide with cobalt carbonate to 1100° with KCl as flux. The cobalt is in bivalent form and the CoO : ZnO ratio is 1 : 4·8, or perhaps 1 : 5. All this, however, does not have any bearing on the vital question as to whether, in these crystals, one has to do with a chemical individual or only a solid solution. A little more progress seems to be made by Burgstaller (*Chem. Zentr.*, 1912, II., 1523), who, noting the fact that the colours in question are blue, red, or green, considers that we are dealing in the blue and red with solid solutions which show the usual colours of cobalt in solution. In the green with ZnO we have blue on a substratum of yellow. While ZnO is white at ordinary temperatures, when heated it passes into a yellow modification, and it seems that in the presence of CoO the reversal into white on cooling is prevented. If this theory is true it would seem possible by carefully choosing conditions to obtain a blue colour with zinc. Burgstaller's ratio of CoO to ZnO in his Rinmann's green was 7·05 : 100, very different from that of Hedvall.

The work of Levy (*Proc. Chem. Soc. London*, xxviii., 91) on the cyano-platinites has confirmed Hadow's explanation of the action of bromine on these salts, except that the formula of the brown salt should be 6 $K_2Pt(CN)_4.K_2Pt(CN)_4.Br_2$, instead of 5 molecules of the unoxidised salt, as Hadow thought. Levy also oxidised the cyano-platinite by MnO_2 or PbO_2 in sulphuric acid solution, obtaining a similar compound to that obtained by the action of bromine. It thus seems that $(7K_2Pt[CN_4])$ is capable of acting as a feebly positive bivalent base. More interesting were the results obtained by oxidising the cyano-platinite with hydrogen peroxide, especially in the form of "perhydrol," when salts of the type M' Pt $(CN)_4$ (simple and double) are formed. These seem evidently to be salts of trivalent platinum, and to have the composition which may be expressed by $MCN.Pt(CN)_3$. In the discussion which followed the reading of this paper, Professor Reynolds called attention to a lithium salt in his laboratory which seemed to have the composition $Li_2Pt(CN)_5.2H_2O$, which might be $2LiCN.Pt(CN)_3.2H_2O$. Further work on these salts will be awaited with interest.

(To be continued).

THE ELECTROLYTIC REDUCTION OF IRON FOR ANALYSIS.

By J. C. HOSTETTER.

In the view of the ease with which reductions can be carried out electrolytically, it is surprising that this subject should have been so neglected in the field of analytical chemistry. The electrolytic reduction of iron for subsequent titration seems to have attracted little attention. (The only work hitherto undertaken from this viewpoint which has come to the attention of the writer is a paper offered by H. C. Allen at the Rochester meeting of the American Chemical Society, September, 1913. The paper was read by title only, and appears not to have been published). With other ends in view, ferric salts have often been reduced by this means.

This method has been investigated to some extent by the writer for the specific purpose of subsequent titration, and has been employed by him at intervals during the past year. Since the method is entirely practicable and occasionally very desirable, it may not be amiss to call attention to the conditions to be controlled when this method is used for analytical purposes and to indicate the degree of accuracy of which it is capable.

The optimum conditions for complete reduction are primarily those which lessen the formation of oxidising compounds by the current. The most suitable electrolyte for this particular problem is dilute sulphuric acid. The temperature during electrolysis should be above 60° C. and the current density low. These conditions are unfavourable to the formation of both hydrogen peroxide and persulphuric acid (for discussion of these conditions see

Gmelin-Kraut Handb. d. Anorg. Chem., 7th Auf., Bd. I, Abt. i., 128, 558). The amount of peroxide formed at the cathode by the action of nascent hydrogen on oxygen diffusing from the anode depends partly on the cathode material (M. Traube, *Ber.*, 1882, xv., 2434). Thus Pd, under given conditions, yields most hydrogen peroxide, Pt and Hg come next, while metals which do not readily absorb hydrogen, as Au, Ag, Zn, Cu, and Pb, yield but very little. With oxidisable anodes, such as Mg, Zn, &c., hydrogen is the sole product of the anode (*cf.*, Elsasser, *Ber.*, 1876, ix., 1818; 1878, xi., 587). In the presence of ferrous sulphate, however, the amount of hydrogen peroxide formed in the cathode chamber must necessarily be low. With the reducing action of the current any peroxide would oxidise the ferrous sulphate to ferric, and this in turn would be reduced by the current. This was tested out experimentally with 1 mgrm. of iron present and found to be true. Therefore, the time of electrolysis after complete reduction can produce no excess consumption of permanganate due to peroxide formation.

Considering the above facts, it was decided to use a gold dish of 800 cc. capacity as cathode (effective surface, 200 sq. cm.). Inasmuch as soluble anodes yield no oxidising materials in the solution, Mg and amalgamated Zn anodes were first employed. By this means the reduction is made very rapid, and the use of a porous cell around the anode is dispensed with. Since, however, it is difficult to obtain these metals free from impurity, such as iron—thus introducing a correction—the use of soluble anodes was abandoned and a Pt anode with porous cell substituted.

The use of a porous cell as an anode chamber introduces two sources of error:—(1) The absorption of iron salt by the cell itself; (2) diffusion of iron into the anode chamber, where it is immediately oxidised. The first is probably negligible since the cell "seasons" rapidly. The second is made negligible in the following manner. When the reduction is complete in the cathode chamber—as shown by test for ferric iron with thiocyanate—the current is stopped, the contents of the anode chamber poured into the cathode chamber, and, after filling the anode chamber with fresh acid, the current is allowed to run some five to ten minutes longer until the last of the iron is reduced. In this manner the iron left in the anode chamber at the end of the electrolysis is reduced to 0·1 to 0·3 mgrm. A syphon connecting the two chambers was also employed to lessen this diffusion. The large currents, however, caused so much heating in the syphon tube that its use was abandoned in favour of the above scheme.

TABLE I.—*Ferrous Ammonium Sulphate.*

Amount of salt. Mgrms.	Grms. $KMnO_4$ solution (0·1 N). Titrated directly.	Reduced electrolytically after oxidation.
3000	89·53	89·43
3000	89·44	89·40
3000	89·47	—

TABLE II.—*Electrolytic Reduction of Ferric Ammonium Sulphate Solution.*

Fe present. Mgrms.	Time of reduction. Mins.	Volts.	Ampères.	Fe in anode chamber. Mgrm.	Fe in 1 grm. solution.
570	780	2·5—8·5	0·35—8·5	0·29	0·005693
570	79	6·0—7·0	8·0—10·0	0·11	0·005696
570	109	4·5—9·0	4·8—10·0	0·22	0·005690
150	60	6·5—10	8	0·15	0·005709
570 }		Reduction with zinc			{ 0·005702
570 }					{ 0·005695
570		Reduction with SO_2			0·005684

Of the materials tested for suitability as porous cells, the unglazed Marquardt porcelain crucibles (20 cc.) seem to answer best. To keep spray from the anode out of the cathode chamber, the top of the crucible is covered with a funnel of the same diameter. The anode lead is brought down through the stem. The funnel is clamped over the crucible with a frame of glass rod; tension is secured with rubber bands. Oxygen escapes through a lateral hole in the funnel stem. The anode is of Pt foil with an effective area of some 28 sq. cm.

The Method.—The ferric (sulphate) solution (volume 300 cc.) is placed in the gold dish (cathode) and 10 cc. sulphuric acid (1·84) added. The anode chamber is filled with acid (1 : 30), the anode inserted, and electrolysis started. The temperature is raised to 80° C. The current employed is about 8 ampères, while the voltage drop across the cell is 8 volts. Under these conditions 0·5 grm. iron is reduced to the ferrous condition in sixty to seventy minutes. After a drop test with thiocyanate shows that reduction in the cathode chamber is complete the current is stopped, the anode chamber acid is added to the main solution, and, after re-filling the anode chamber, the electrolysis is continued ten minutes. At the end of this time the cathode liquid is titrated with permanganate.

It will be seen that the method as carried out is not particularly rapid. On the other hand, its favourable features are:—(1) Nothing is introduced into the solution that may carry impurity; and (2) conditions need be defined only within wide limits. The accuracy of the method can only be determined by more extensive comparison with reductions by other methods. The precision attainable under the best conditions is shown in Tables I. and II. Under ordinary conditions a precision of better than 1 part in 200 or 300 can not be expected until after the method has been more completely developed.—*Journal of the Washington Academy of Sciences*, iii., No. 16.

THE

PREPARATION OF SELENIC ACID AND SODIUM SELENATE FOR USE AS REAGENTS IN THE DETERMINATION OF BROMINE IN HALOID SALTS.

By PHILIP LEE BLUMENTHAL.

SELENIC acid and sodium selenate have been proposed in a previous paper from Kent Chemical Laboratory, Yale University (Gooch and Blumenthal, *Am. Journ. Sci.*, xxxv., 54) as reagents for the qualitative elimination of bromine, in determinable form, from haloid salts. These reagents when made by ordinary methods (Gmelin-Kraut, "Handbook,"-*Anorg. Chem.*, 1907, i., 769) may contain contaminating material likely to be objectionable. The following methods have therefore been devised for the preparation of these reagents in such condition that any foreign material remaining in them shall not interfere with the success of the analytical process.

Selenic Acid.

The method proposed for the preparation of selenic acid depends upon the action of nitric acid and potassium bromate upon selenious acid, the bromic acid formed reacting with the selenious acid according to the following equation: $3H_2SeO_3+HBrO_3=3H_2SeO_4+HBr$. Further action of the bromic acid breaks up the hydrobromic acid, according to the equation $HBrO_3+5HBr=3Br_2+3H_2O$. Upon evaporating the solution to low volume, a second liberation of bromine accompanied by nitrogen oxides takes place, apparently according to a reaction like the following:— $2HBrO_3+2HNO_3=2H_2O+Br_2+2NO_2$. The free bromine and the nitrogen oxides are, of course, easily volatilised. The preparation of selenic acid based upon these reactions was put to the test as follows:—

Preliminary Test.—Selenious acid was prepared by dissolving elementary selenium in nitric acid, and evaporating the solution to dryness. The crude selenious acid so

obtained was sublimed from manganese dioxide according to the method used by Norton (*Am. Journ. Sci.*, [4], vii., 290), and the thin needle-like crystals were bottled as rapidly as possible. A solution convenient for use was made by dissolving 2 grms. of the purified selenium dioxide in 200 cc. of water and a portion of 20 cc., containing 0·1 grm. of the dioxide, was used for each test. To each portion contained in an Erlenmeyer flask were added 10 cc. of 1·1 nitric acid and a little potassium bromate, and this solution was evaporated to a low volume. When barium nitrate was added to the concentrated solution, and the free acid nearly neutralised with ammonium hydroxide, white barium selenate was precipitated. Though impure on account of its tendency to occlude foreign material, this precipitate proved to be practically free from selenious acid.

Preparation of the Reagent.—To 10 grms. of selenium dioxide dissolved in 75 cc. to 100 cc. of water were added 6 grms. of potassium bromate and 4 cc. of strong nitric acid. This mixture was heated on the water-bath until perfectly colourless. After the second evolution of bromine, which occurred when the volume was quite low, a little more bromate was added to decompose the excess of nitric acid, and the heating was continued. When the addition of a crystal or two of bromate caused no further evolution of bromine, the colourless solution was made slightly ammoniacal, heated to the boiling-point, and treated with a hot dilute solution of barium nitrate. The precipitated barium selenate, after settling, was filtered with suction, washed thoroughly with hot water, and finally transferred to a large crucible and dried at low redness. The weight of this product was about 25 grms., while the theoretical amount obtainable from the selenious acid taken was about 25·1 grms. After weighing, the selenate was treated in a porcelain crucible with 5 cc. of strong sulphuric acid (sp. gr. 1·8°) and some 20 cc. of water. The pasty mass so obtained was heated about two and one-half hours on the water-bath, and finally diluted, filtered, and washed. The filtrate and washings were made up to 1 litre, and an aliquot was taken for analysis by the method of Pierce (*Am. Journ. Sci.*, [4], l., 416). This analysis showed about 94 per cent of the selenium taken to be present. From the determination of the selenious acid present by the method of Gooch and Clemons (*Ibid.*, [3], l., 51) it was found that 85 per cent of the selenium was present as selenic acid, the presence of selenious acid in the final product being due in this case to the fact that the barium precipitation was made in alkaline solution, under which conditions barium selenite is also precipitated. The total yield of selenic acid was 78 per cent of the theoretical. Later experiments have shown that the contamination by selenious acid may be to a large extent avoided by precipitating while the solution still contains free nitric acid.

Sodium Selenate.

The preparation of sodium selenate, to be used with sulphuric acid in place of free selenic acid, was also investigated.

Preliminary Test.—Elementary selenium (1 grm.) was fused in platinum with sodium peroxide (2 grms.) and sodium carbonate (6 grms.). The mass, after dissolving in water and filtering, barely bleached a few drops of dilute permanganate, showing that the selenium had been oxidised almost completely to selenic acid, only a little selenious acid remaining.

Next, the finely-powdered metal (1 grm.) was fused with sodium peroxide (5 grms.) in a nickel crucible, and after cooling, the melt was partially neutralised with sulphuric acid to facilitate the analysis, and filtered. The filtrate and washings were made up to 100 cc., and 10 cc. of this solution were analysed by the method of Gooch and Scoville (*Am. Journ. Sci.*, [3], l., 402). Two analyses showed the yield to be fairly quantitative and suitable for the analytical elimination of bromine.

Preparation of the Reagent.—In utilising the method on a larger scale, about 105 grms. of powdered selenium and 500 grms. of sodium peroxide were thoroughly mixed and fused in charges containing 10 grms. to 15 grms. of selenium, nickel crucibles being employed. The reaction was rapid, and a few minutes' heating over a Bunsen burner sufficed to bring the mass to liquid condition. After cooling, the crucible was placed in a beaker of cold water, and covered with a watch-glass to avoid loss by spattering. The melt dissolved with great evolution of heat, and cold water was added from time to time to prevent boiling. Some finely-divided material remained floating in the strongly alkaline liquid. A slight green colour, probably due to the solution of small amounts of nickel, was also noticed. The solution could not be filtered through paper, and a platinum cone, lined with asbestos, was utilised, although the process was exceedingly laborious. The opaque filtrate consisted chiefly of sodium selenate and sodium hydroxide, with some sodium carbonate due to contact with the air.

In order to purify the selenate from sodium hydroxide, the attempt was first made to remove the latter by shaking the solution with alcohol. This procedure was found to have several disadvantages. The amount of time involved, the inconvenience of handling large quantities of strongly alkaline solution, and the not inconsiderable amount of carbonate formed, all militate against the process. But the greatest disadvantage lies in the fact that the dissolved carbonate and selenate of the lower aqueous layer are very difficultly crystallised. The successful method of purification ultimately developed consisted in evaporating the alkaline liquid to a pasty condition over a free flame, and removing as much caustic alkali as possible by continued extraction with alcohol which had been distilled from lime (97 to 99 per cent pure). The extraction was hastened by warming on the steam-bath, but in this latter treatment red amorphous selenium was formed by reduction of the solution. Six or eight extractions sufficed to remove most of the hydroxide.

The residue, consisting chiefly of sodium selenate and sodium carbonate, could not be crystallised from water. It was found necessary to convert the carbonate to sulphate in order to obtain crystallisable material, and after careful neutralisation with sulphuric acid, the mixture of sulphate and selenate was crystallised by repeated evaporations. The sulphate tends to crystallise first, and a partial separation may be accomplished in this manner. The mixed crystals of sodium selenate and sulphate first obtained were quite efflorescent, but on warming and evaporating to greater concentration, crystals of a lower order of hydration were obtained. The selenate and sulphate can also be thrown out by alcohol, but this method was not satisfactory and was discarded.

The several crops of crystals were combined, filtered on a Buchner funnel with suction, well-drained, and finally the mass was heated to 108° C. for some hours, whereby most of the water was driven out, and a mixture of nearly anhydrous sodium salts was obtained. Analysis of the mixed product showed it to average about 65 per cent of selenate, and the total yield of sodium selenate was about 58 per cent of the theoretical amount. Considerable material was lost in the preliminary attempts at purification, in the tests made from time to time, and in the mother-liquor from the crystallisations.

This material thus prepared is serviceable for immediate use with sulphuric acid in the method proposed for the separation of bromine and chlorine, and no attempts were made to separate the sulphate and selenate completely. In view of experience obtained in this work, it seems probable that by rapidly evaporating the filtered solution of selenate and hydroxide over a free flame, and rapidly extracting the residue with absolute alcohol, the carbonate formation may be, to a large degree, inhibited. This, of course, reduces the amount of sulphate ultimately formed, since the greater part of the alkali, excepting the carbonate, is removed by the alcohol treatment. The resulting aqueous solution,

containing a small amount of sulphate, but no selenite, can be purified fairly well by fractional crystallisation, as the selenate is more soluble in water than the sulphate.

It is to be noted that sodium selenate may also be prepared by fusing with sodium carbonate the barium selenate obtained in the process previously described for making selenic acid, the amount of carbonate taken being less than that required to decompose the barium salt completely. Upon extracting the product with water the sodium selenate dissolves, and may be crystallised from the filtered solution.

The processes described afford easy means for preparing selenic acid and sodium selenate in such condition that, though these products are not pure, they are suitable for use in the quantitative elimination of bromine from haloid salts according to the methods to which reference has been made. —*American Journal of Science*, xxxv., p. 93.

THE SCIENTIFIC WEEK.

(*From Our Own Paris Correspondent*).

THE BURNS FROM THE X-RAYS.

A somewhat prolonged manipulation of the X-rays occasions too often, alas! very serious accidents that are sometimes fatal. As a means of protection it has been considered advisable to use gloves of a special kind absorbing 60, 75, and even 80 per cent of the X-rays. But the hard rays were hardly ever absorbed. Dr. Maxime Menard, head of the service of radiology at the Cochin Hospital, has just devised an efficacious method of protection against the attacks of the X-rays. A special kind of chest or cupboard, composed of three panels, lined inside with a sheet of lead, of which the minimum thickness is 4 mm., protects the specialist in radiology. Crookes's tube producer of the Röntgen-rays and the patient who is to undergo the treatment of the radiations are placed inside this cupboard. The protecting gloves are formed of a rubber tissue in which have been incorporated salts of lead and sulphate of baryta. These metallic salts totally absorb the X-rays when in suitable proportion. The thickness of the tissue does not exceed 4 mm. The gloves are rather heavy, but they can nevertheless be easily managed. The experiments made by Dr. Menard in the most variable conditions have shown that the protection of the radiologist and his assistants against the X-rays was absolute.

THE PROTECTION OF BUILDINGS AGAINST LIGHTNING.

The electrical atmospheric discharges to which a building is exposed are of two sorts. The first results from the gradual increase of potential between the cloud and the building; when this difference is sufficient to overcome the critical resistance of the air interposed, the discharge takes place; this discharge, generally oscillating, is regulated by the known laws of electricity relating to resistance, inductance, and capacity. The second sort is a violent secondary discharge which is produced in the neighbourhood; it is hardly influenced by ordinary lightning conductors, and to protect the building with them the roof would require to be largely covered with metal. Lightning discharges are oscillating, and the oscillations are exceedingly frequent, from 100,000 to perhaps several millions of periods to the second. Now the electric constants of these conductors are entirely different to those frequencies to what they are normally; the impedance especially is considerable. Little is known concerning the electrical conditions of atmospheric discharges. Generally the discharges between the clouds and the earth are of a very high voltage, and consequently put a considerable energy in movement. This energy is transformed partly into Joule heat and partly into electric radiation emitted in the form of waves. The fraction of energy thus radiated depends upon a crowd of circumstances, particularly it increases with the frequency. If the discharge takes place between the cloud and a thin rod of copper, for a frequency of a million periods, it is calculated that the quantity of energy radiated may be fifty times greater than that transformed into heat. Nevertheless there is always uncertainty as to the amount of frequency. If it is admitted that the discharge after having reached the rod of the conductor is influenced by the characteristics of this rod, the length of the rod for a height of 15 metres would give frequencies of the order of five millions. If, on the contrary, it is considered that the length of the wave is regulated by the distance of the cloud from the earth, the frequency would be much lower, 250,000 periods, for example, for clouds at 600 metres. In order to render good service, the lightning conductors must be well installed. If not they are more dangerous than useful. A lightning conductor of great height and with some defect (such as wire broken at one point, badly joined, or badly set into the ground) may attract dangerous discharges on to the house. It is necessary to supply the building that is to be protected from lightning with a large number of rods, which seems to assure the best outlet for the secondary discharges; six for a house of 30×15 metres are not too many. These rods must be placed outside the house, and as much as possible isolated from all the metallic canalisations of the building. In town it is good to employ copper rods for lightning conductors. In the country galvanised iron may be employed; it is advisable to give it the form of a cylinder or a tube.

DISTILLATION OF COAL AT A LOW PRESSURE AND LOW TEMPERATURE.

M. A. Pictet and M. Bouvier, of Geneva, have just made a series of interesting experiments. By distilling coal in vacuum, without exceeding 450°, these two *savants* have collected a cold condensed liquid (1·5 per cent of the weight of the coal) and a tar (4 per cent), and no ammonia. This tar, called vacuum tar, is very different from ordinary tar. It is light brown, and does not contain any phenol, but merely bases. After a washing with alkali and acids, if it is made to undergo another distillation, slightly fluorescent liquids appear, very much resembling petioles, then products of turpine and menthol. The oxidation of these products only give acids of an oily nature. In these tars we find neither naphthaline nor anthracine, nor any aromatic body. If this vacuum tar is passed through a red-hot tube then there will appear:—(1) Lighting gas; (2) strongly ammoniacal substance; (3) ordinary tar, charged with phenol, benzine, and anthracine. The pyrogenous distillation of coal is then made in two operations, and the formation of the latter products is preceded by the formation of vacuum tar. This study is of the greatest interest as far as concerns the possible genesis of natural petioles.

Royal Institution.—A General Meeting of the Members of the Royal Institution was held on the 3rd inst., the Duke of Northumberland, President, in the Chair. It was announced that the Eighty-eighth Christmas Course of Juvenile Lectures, founded at the Royal Institution in 1826 by Michael Faraday, will be delivered this year by Prof. H. H. Turner, D.Sc., D.C.L., F.R.S., Savilian Professor of Astronomy in the University of Oxford, his title being "A Voyage in Space." The Lectures will be experimentally illustrated, and the subjects are as follows:—"The Starting Point—Our Earth," Saturday, December 27, 1913; "The Start through the Air," December 30; "Journeying by Telescope," January 1, 1914; "Visit to the Moon and Planets," January 3; "Our Sun," January 6; and "The Stars," January 8. The lecture hour is 3 o'clock.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, November 6th, 1913.

Sir ARCHIBALD GEIKIE, K.C.B., President, in the Chair.

PAPERS were read as follows:—

"*Studies in Heredity. II. Further Experiments in Crossing the British Species of Sea Urchins.*" By Prof. E. W. MACBRIDE, F.R.S.

In this paper the results obtained two years ago and communicated to the Society are confirmed and extended. The hybrid produced by fertilising the egg of Echinus with the sperm of Echino-cardium is described. This hybrid was not obtained two years ago. The effect of foreign sperm in producing cytolysis on an egg is described, and it is also shown that an egg may become totally unreceptive for foreign sperm whilst it is still perfectly capable of being fertilised with the sperm of its own species.

"*Soil Solution and the Mineral Constituents of the Soil.*" By A. D. HALL, F.R.S., W. E. BRENCHLEY, and L. M. UNDERWOOD.

"*Synthesis by Sunlight in Relationship to the Origin of Life.—Synthesis of Formaldehyde from Carbon Dioxide and Water by Inorganic Colloids acting as Transformers of Light Energy.*" By Prof. B. MOORE, F.R.S., and T. A. WEBSTER.

"*Trypanosomes causing Dourine (Mal de Coït or Beschälseuche).* By B. BLACKLOCK, M.D., and W. YORKE, M.D.

"*Postural and Non-Postural Activities of the Mid-Brain.*" By T. G. BROWN.

"*Nature of the Coagulant of the Venom of* Echis carinatus." By J. O. W. BARRATT.

"*Morphological Studies in the Benzene Series. IV. The Crystalline Form of Sulphonates in Relation to their Molecular Structure.*" By E. H. RODD.

"*Structure of the Diamond.*" By Prof. W. H. BRAGG, F.R.S., and W. L. BRAGG.

"*Electric Discharge Phenomena in Rotating Silica Bulbs.*" By Hon. R. J. STRUTT, F.R.S.

"*Origin of Thermal Ionisation.*" By J. N. PRING.

"*Refraction and Dispersion of Gaseous Nitrogen Peroxide.*" By CLIVE CUTHBERTSON and MAUD CUTHBERTSON.

THE NEW COUNCIL.

THE following is a list of those who have been recommended by the President and Council of the Royal Society for election into the Council at the anniversary meeting on December 1:—

President—Sir William Crookes, O.M., F.R.S.

Treasurer—Sir Alfred Kempe, M.A., D.C.L.

Secretaries—Sir John Bradford, K.C.M.G., M.D., D.Sc., and Prof. Arthur Schuster, Sc.D., Ph.D.

Foreign Secretary—Dukinfield Henry Scott, M.A., Ph.D., LL.D.

Other Members of the Council—The Right Hon. Arthur James Balfour, D.C.L.; Prof. William Maddock Bayliss, D.Sc.; Frank Watson Dyson, LL.D.; Henry J. H. Fenton, Sc.D.; Prof. William Gowland, D.Sc.; Frederick Gowland Hopkins, D.Sc., M.B.; Sir Joseph Larmor, D.Sc.; Prof. Charles H. Lees, D.Sc.; Prof. Ernest William MacBride, D.Sc.; Prof. Grafton Elliott Smith, M.D.; Prof. James Lorrain Smith, M.D.; Sir John Thornycroft, LL.D.; Prof. William Whitehead Watts, Sc.D.; Alfred North Whitehead; Charles T. R. Wilson, B.Sc.; Arthur Smith Woodward, LL.D.

PHYSICAL SOCIETY.

Ordinary Meeting, October 24th, 1913.

Prof. C. H. LEES, F.R.S., Vice-President, in the Chair.

A PAPER entitled "*The Ice Calorimeter, with Remarks on the Constancy of the Density of Ice,*" was read by Mr. EZER GRIFFITHS.

The primary object of the work was the re-determination, by an electrical method, of the constant of Bunsen's ice calorimeter. The heat was supplied by a manganin coil wound on a mica rack which fitted the interior tube of the calorimeter, and the results are based on determinations of E.M.F. and resistance. The current was adjusted so that the difference of potential at the ends of the heating coil was exactly equal to the E.M.F. of a number of standard cadmium cells in series.

The conditions were varied as much as possible. Thus the rate of energy supply in the fastest experiments was more than seven times that in the slowest.

Errors due to progressive freezing or thawing of the ice mantle were greatly diminished by suspending the calorimeter within a transparent vacuum vessel of cylindrical form, the stem and capillary of the calorimeter projecting through a rubber stopper, and the vacuum vessel being completely embedded in powdered ice.

The mean value of the calorimeter constant was found to be 15 486 mgrms. of mercury per mean calorie.

The Constancy of the Density of Ice. Various observers have advanced evidence tending to show that the density of ice at 0° C. is not a definite constant. A consideration of their work leads to the conclusion that the small variations of density found for different samples might be simply due to the presence of occluded water or an amorphous modification cementing the ice crystals together.

The value (80·30) of the latent heat of fusion of ice, calculated from the ice calorimeter, supports this view, as it is higher by about 0 7 per cent than the value obtained by direct determinations with ice in bulk.

DISCUSSION.

Prof. H. L. CALLENDAR noted with pleasure that the author had very closely verified Dieterici's value, using an entirely different method. He had had occasion to look into Dieterici's determinations in connection with the specific heat of water, and thought them very reliable. They agreed very closely indeed with the results obtained by Dr. Barnes and himself by the continuous electric method. The most uncertain element in Dieterici's work was the thermal capacity of his silica bulb, which amounted to about 25 per cent of the whole. The extreme uncertainty of the calculation of latent heat from the volume changes on melting was not, perhaps, sufficiently realised. The calculation depended on the *difference* of the specific volumes of ice and water, so that any error in the value assumed for the density of ice seriously affected the value obtained for L. Thus the author, taking Vincent's result for the density of ice (=0·9161 grm. per cubic centimetre), had calculated L = 80·3 *mean calories*, whereas, if 0·9167, the density as given by Barnes, had been assumed 79·5 (approx.) would have been obtained for the latent heat.

Dr. J. A. HARKER mentioned a possible error due to the suction of mercury at atmospheric temperature, through a capillary of varying temperature, into the body of the calorimeter. Was the author's method of getting rid of "drift" superior to the method of putting one calorimeter inside another and larger one, and, by varying the pressure on the ice in the second one, adjusting its temperature until the "drift" was zero? He had at one time tried glacial acetic acid instead of ice. It had the advantage that when heat was supplied mercury was pushed out instead of sucked in. Also the transition temperature was between 16° C. and 17° C., and the constant was about 30.

Mr. F. E. SMITH referred to the question of the leads to the coil. If they were too thick too much heat was conducted along them; if too thin too much heat was pro-

duced in them by the current. If the cross-section was assumed to be 2 sq. mm. then the resistance of a pair of manganin leads, each of which was 25 cm. long, would be 0·1 ohm. Since the heating coil was of 20 ohms resistance it followed that the heat produced in the leads was 0·005 times that produced in the coil. This heat was not accounted for in the calculations, and he would be glad if Mr. Griffiths would state what became of it. In his opinion much of it passed into the oil in the calorimeter. The experiments made by the author did not appear to him to indicate the magnitude of the effect, since the heat passing from the leads to the oil would be proportional to the time of an experiment and also to the square of the current used.

Prof. Silvanus Thompson asked whether there was any evidence of an allotropic or amorphous form of ice. According to the theory of crystal formation by arrangements of densest packing of molecules, any amorphous form should be less dense (as is the case of fused silica as compared with quartz crystal) and its specific heat per unit mass should be greater. Was the author sure that the water used was perfectly air-free?

Prof. C. H. Lees said the author had raised his opinion of the ice-calorimeter. He would like to know where it now ranked in the author's own estimation among other instruments used for similar purposes.

The Author agreed that the calculated value of the latent heat must be accepted with reserve, as it was difficult to predict in what direction the assumed value of the density of ice might be in error. The presence of occluded water in the specimens used would make the value too high, while minute air bubbles, due to dissolved air separating out, would make it too low. He had not yet attempted the substitution of other substances for ice. The use of glacial acetic acid would obviate the trouble at the orifice, since mercury would be ejected instead of sucked in. The heating coil was so designed that the heat generated in the leads was small. Moreover, only a fraction of this would pass into the bulb of the instrument, since the coil proper extended nearly the entire length of the inner tube. The heat generated in the leads outside the bulb would be partially absorbed by the glass stem and the air surrounding the leads. The slight conduction by the glass stem and leads down to the bulb would cause a minute "drift" lasting for a considerable time after switching off the heating current. This was corrected in the manner indicated in the paper. He regarded the variation of the density of ice to be due to occluded water and not to allotropic crystallisation. He considered the water to be present as an amorphous cement binding the crystals together. In reply to Prof. Lees, he considered electrical methods, as, for example, the continuous electric method of Prof. Callendar, superior to the ice calorimeter. One advantage of the latter was, however, that there was no radiation correction.

A paper on "*An Electrostatic Oscillograph*," by Messrs. H. Ho and S. Koto, was read by the latter.

The paper describes an electrostatic oscillograph suitable for recording very high voltages. Two vertical bronze strips pass symmetrically between two parallel metallic plates called "field plates." They are connected at their lower ends by a silk fibre which passes under an ivory pulley. An extremely small mirror is fixed to the strips. This arrangement constitutes the vibrator, which, mounted on an ebonite frame, is immersed in an oil bath. To the upper extremities of the strips are connected the terminals of a direct-current voltage of about 300. The alternating voltage to be recorded is connected to the "field plates," in parallel with which there are two oil condensers in series. The electrical midpoint of the direct-current battery is connected to a point between the condensers.

The turning moment on the strips is proportional to the product of the momentary values of the alternating-current voltage and the direct-current voltage, so that if the latter is constant, the deflection of the mirror accurately follows the variation of the former.

Oil plays an important part, not only acting as a damping agent and insulator, but increasing the sensitiveness on account of its high dielectric constant.

In cases where voltage is low, but the source of energy is so limited that a sufficient current cannot be taken to actuate the ordinary oscillograph, the electrostatic vibrator may be used by applying the voltage in question to the strips, while the terminals of a high-tension battery, or influence machine, are connected to the "field plates." The instrument may also be used for recording very small currents by replacing the oil condensers by two exactly equal resistances, which are traversed by the current.

Discussion.

Mr. A. Campbell thought it was a considerable advantage to be able to do without high resistances. Dr. G. W. C. Kaye had suggested to him that the instrument might be of great use in work with X-rays and in other cases where the charge was being taken from an induction coil.

Mr. R. S. Whipple emphasised the commercial advantage of the instrument. High resistances were very expensive. Einthoven was the first to propose an electrostatic oscillograph, and a Belgian inventor had constructed an instrument similar in principle.

Prof. G. W. O. Howe stated that in the two curves given the difference was assumed to be due to a "lead" in the electromagnetic instrument. Was there any actual evidence that it was not due to "lag" in the other? If the oil did produce a phase-difference, it would introduce a "lag" and give the observed effect.

Mr. E. H. Rayner pointed out how, by suitably altering the arrangement of Fig. 8 in the paper, the instrument could be used as a wattmeter.

Mr. J. T. Irwin said he was already aware of the device suggested by Mr. Rayner, having described it in 1907. The principal difficulty with an electrostatic oscillograph was that a very high polarising voltage is required if the zero is to be stable. The authors had reversed the process —using a small polarising voltage compared with the alternating-current voltage. Hence it is only when the alternating-current voltage is applied that a change of zero is produced. In most cases this cannot be compensated beforehand, as we do not know the value of the potential to be applied. Castor oil was not suitable for use in oscillographs, as it became acid and conducting under high voltages. Well-filtered paraffin had not this defect.

Mr. D. Owen regretted that the paper contained so little in the way of actual work accomplished with the instrument. If one took the values stated in the paper for the inductance of the high resistances used with E.M. oscillographs, and assumed a frequency of 100 vibrations per second, calculation seemed to show that the phase-differences introduced by the use of such resistances were much too small to account for the discrepancies in the experimental curves.

Mr. G. L. Addenbrooke said that if castor oil free from dust and moisture were used he did not think oscillograms with the instrument would be affected perceptibly by action in the oil at 40 periods or higher. With a dry oil much lower periodicities might be used. The influence of moisture is greater with mineral oils than with castor. The dielectric strength varies almost directly with the percentage of moisture present.

Prof. Koto, in reply, said that the frequency of the voltage used for the tests was 60 vibrations, the records being taken on a falling-plate camera. He saw no objection whatever to the use of the oscillograph as a wattmeter, as suggested by Mr. Rayner and carried out by Mr. Irwin. He stated that the oil used was that supplied by the Cambridge Scientific Instrument Co., and that from some rough measurements he had made he found it to have a specific inductive capacity of about 2. The deviation of the strips from the centre was a cause of the change of zero, as Mr. Irwin suggested, if a large polarising voltage be applied. To suppress this effect the authors made the distance between the two field plates, conse-

quently the distance between the strip and the plates, sufficiently great to make this inevitable slight deviation from the centre a very small percentage of the distance between the strip and the plates, and consequently this deviation from symmetry would cause no appreciable "out of balance" of the forces due to the polarising voltage acting upon the strips and effecting this change of zero. Referring to the effect of the oil on the phase relationship of the curves, Prof. Koto stated that he had no doubt that the curves obtained on the electrostatic oscillograph and reproduced in the paper were correct, but he intended to make a series of experiments on different oils to see whether any serious phase differences are caused by the oils having different dielectric hysteresis constants.

NOTICES OF BOOKS.

Principles of Agricultural Chemistry. By G. S. Fraps, Ph.D. Easton, Pa.: The Chemical Publishing Co. London: Williams and Norgate. 1913.

The greater part of this book is devoted to the consideration of the plant, its growth, its relations to the soil, and to the atmosphere, its composition, &c., while questions connected with the feeding of animals are treated rather more briefly. The author quite wisely does not attempt to explain the elementary principles of chemistry, but supposes his readers to possess a fair knowledge of them, and confines himself to the discussion of their applications to the problems of agriculture. Much of his information he has brought together from the valuable bulletins of the American state experimental stations, and although he by no means neglects the work that has been done in other countries and frequently refers to the researches carried out at the Rothamsted and Woburn stations, for instance, the book has more value for the American than for the English agriculturist, since the examples and illustrations are drawn mostly from American practice. On the other hand, the author shows marked skill in the clear summarisation of the essentials of a subject, and the terseness of the style of the text is a commendable feature.

Merck's Reagenzien-Verzeichnis. ("Merck's Index of Reagents"). Third Edition. Berlin: Julius Springer. 1913.

This index is so well known as an almost indispensable aid in analytical and microscopical work that it is doubtless supererogatory to call attention to its merits. In the third edition the arrangement of the second edition is unaltered, but the latter has been revised and considerably enlarged, and in the appendix some details of new reactions and reagents which have been published during 1912 and the present year are included.

Bewährte Arbeitsweisen der Metallfärbung. ("Tested Methods of Colouring Metals"). By Prof. Dr. Ernst Beutel. Wien und Leipzig: Wilhelm Braumüller. 1913. (Mk. 1.80).

This little book will serve as a useful laboratory guide for those who want accurate and clear directions for the colouring of metals. Only well-tested methods, and such as the author has found to be thoroughly reliable in his long experience of such work, are described, and none but the simpler processes, which can be carried out with comparatively cheap materials and without elaborate apparatus, are included. Twenty methods only are chosen for description, but they have been selected so as to be as typical as possible. Some notes are given on the chemical aspects of the operations described, but the worker who has no knowledge of science should be able to get quite satisfactory results if he follows the directions, and his needs are often taken into special consideration, as, for example, in the tables giving the common and scientific names of all the chemicals employed.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Academie des Sciences. Vol. clvii., No. 11, September 15, 1913.

This number contains no chemical matter.

Bulletin de la Société Chimique de France. Vol. xiii.-xiv., No. 16—17, 1913.

Heat of Formation of Silicon Nitride.—Camille Matignon.—When a mixture of silica and carbon is heated to 1400—1500° in a current of nitrogen the nitride, Si_3N_4, is obtained:—$3SiO_2+6C+2N_2=Si_3N_4+6CO$. It is very difficult to determine the heat of formation of this nitride directly, but it may be calculated if a single state of equilibrium is known, and the specific heats. Employing this indirect method the author has obtained the value 159·3 cal., and although this number cannot be regarded as very accurate, it gives some indication of the order of magnitude of the heat of formation of the nitride.

Rotatory Dispersion of Free 1-Bornyl-xanthogenic Acid.—L. Tchougaeff.—A freshly prepared solution of 1-bornyl-xanthogenic acid is lævorotatory for all wavelengths of the visible spectrum, and moreover exhibits the Cotton phenomenon (abnormal rotatory dispersion), the curve passing through a maximum at about $525\mu\mu$. If, however, the solution is allowed to stand the curve undergoes important changes. The values corresponding to the red part of the spectrum diminish, while those corresponding to the green and blue parts increase, and hence the maximum of rotation is displaced towards the violet part of the spectrum. Thus the abnormal dispersion is gradually replaced by that which is characteristic of borneol. The cause of this phenomenon is the spontaneous decomposition of the acid, according to the equation $C_{10}H_{17}OCSSH=C_{10}H_{17}OH+CS_2$.

Rotatory Dispersion of Derivatives of β-Pinene.—L. Tchougaeff and A. Kirpitcheff.—The rotatory dispersion of nopinone is much greater than that of nopinol, and thus the ketonic group is again accompanied by an abnormal exaltation of the dispersive power. The temperature exercises only a very slight influence on the values of the specific rotatory power. The absorption curve of nopinone exhibits a band the maximum being at about 3550, but nopinol absorbs only the extreme ultra-violet, and shows no characteristic band.

Preparation of Anhydrous Manganese Iodide.—F. Ducelliez.—To prepare manganese iodide the finely-divided metal is covered with dry ether, and dry iodine is dropped in. The reaction begins at once, and the ether boils; it is necessary to cool at first, but afterwards the solution is heated on the water-bath, the ether being condensed by means of a reflex condenser. If excess of metal is used the powdered iodide thus obtained is light enough to be poured off with the ether, and thus separated from the manganese. The iodide is white when freshly prepared, but it turns brown after a time; it is soluble in water, and it combines very readily with gaseous ammonia to give products which the author is investigating.

Preparation and Properties of Basic Copper Sulphate, $CuSO_4.CuO$.—Emm. Pozzi-Escot.—To prepare basic copper sulphate a saturated solution of copper sulphate in commercial formol is prepared and warmed, and potassium bisulphite is added. The bisulphite decomposes the copper sulphate, giving cuprous oxide, which then dissolves in the excess of copper sulphate and re-oxidises. Thus an abundant greenish white crystalline precipitate is obtained. The analysis of this substance gives results which agree very well with the formula $CuSO_4.CuO$. When it is heated in a glass tube it turns yellow, and then fuses to a red liquid which can be kept for some time at this temperature without undergoing decomposition. The

sulphate is insoluble in water, but warm water decomposes it slowly, giving a deposit of oxide. It dissolves immediately in dilute acids and decomposes silver nitrate solution with formation of a mixed compound. In damp air it absorbs a molecule of water and gives a green crystalline compound of formula $CuSO_4.Cu(OH)_2$.

Presence of Boron in Milk and Eggs.—Gabriel Bertrand and Henri Agulhon.—If boron is a fundamental element of the living cell it must exist in the organism from the very beginning, and hence should be found in milk and eggs. The determination of the metalloid in both substances has always given positive results when carried out by the authors, and they consider that boron should be classed with the other catalytic elements of the living cell.

Determination of Tartaric, Malic, and Succinic Acids in Wine.—Paul Dutoit and Marcel Duboux.—To determine tartaric, malic, or succinic acids by the physico chemical volumetric method the diluted solution is treated with a suitable precipitant in small quantities, and after each addition the conductivity is determined. The results are expressed graphically (conductivity as ordinates, reagent as abscissæ), and it is found that the "precipitation curve" thus obtained has a marked inflection at the point at which precipitation is complete. The best reagents to use in the case of the acids in question are the salts of barium and lanthanum. In wines the three acids must first be separated from other substances in solution, the best method being to precipitate with silver nitrate, and dissolve the precipitate in alcoholic sodium bromide or chloride. The sum of the three acids is first determined by the use of the formula $2000 \frac{X \times N}{v}$, where X = number of cc. of reagent corresponding to the point of inflection, N is the normality of the reagent, v is the volume of the solution used. Since the difference of the solubility of the malate and succinate of barium is considerable in a solution containing 60 per cent of alcohol, the same method, using barium acetate as reagent, can be applied to the determination of the tartaric and malic acids, the succinate remaining in solution. Finally, the tartaric acid is determined by using 25 cc. of the solution, 75 cc. of alcohol at 95°, 5 cc. of glacial acetic acid, and precipitating with 0·89 N barium acetate solution.

Determination of Pure Caoutchouc in Raw Caoutchouc.—R. Marquis and F. Heim.—The amount of pure caoutchouc in a raw specimen may be ascertained by dissolving in chloroform, and adding about eight times the weight of pure sulphuric acid. After shaking for three minutes two volumes of alcohol are added, and the whole is allowed to stand for some hours. The flocculent precipitate is then filtered off, washed with alcohol, dried at 100°, and weighed. Its weight is exactly equal to that of the pure caoutchouc present. The formula of the precipitate appears to be $(C_{10}H_{16})_{10}.H_2O$. For the purposes of an exact analysis it is preferable to separate the resin from the raw caoutchouc before applying this method.

MISCELLANEOUS.

Lewis's Quarterly List of New Books and New Editions.—We have received the October number of the additions to Lewis's Technical and Scientific Circulating Library. It contains the books which have been published and added to the Library during the months of July, August, and September. These are not the busiest months for the publisher, and consequently the list does not contain quite so many important works as usual. The first part of the list is occupied with the additions to the medical side of the Library, while in the second, under the general heading "Scientific," will be found those on such subjects as Chemistry, Engineering, Metallurgy, Motor Cars, Technology, &c. Under the last-named, we notice the first volume of the new edition of Lewkowitsch's "Chemical Technology and Analysis of Oils, Fats, and Waxes" is included. Other interesting books are Part VI. of the 3rd edition of Frazer's "Golden Bough" (under "Anthropology"), Reid's "Turbines Applied to Marine Propulsion," Butler's "Portland Cement," Brewer's "Carburation," &c. Short notes are given to the more important works, and the list should be useful to those wishing to see what has appeared during the months included on any subject they are interested in.

Royal Society of Arts.—The Society will commence its 160th Session on November 19 with an Address by the Chairman of the Council, Col. Sir Thomas H. Holdich, K.C.M.G., K.C.I.E., C.B., D.Sc. Before Christmas there will be four meetings besides the opening meeting. The first of these will be devoted to a paper by Dr. Chalmers Mitchell, on "Zoological Gardens"; the second to a paper by Mr. John Umney, on "Perfumery." At the third, Mr. Thorne Baker will read a paper on "Applications of Electricity to Agriculture," and at the last meeting before Christmas, the question of the Channel Tunnel will be brought forward by Mr. Arthur Fell, M.P. A number of papers for the meetings after Christmas have also been promised, but the dates for these are not yet arranged. Amongst them will be a lecture by Sir Sidney Lee, on "Shakespeare's Life and Works," to be delivered under the Aldred Trust, which is intended for the Promotion of Literature as well as Science. There will be five courses of Cantor Lectures. The first, by Prof. Coker, on the "Measurement of Strains in Materials and Structure," will comprise, amongst other matters, the results of his own investigations into the application of polarised light to the measurement of stresses. The second course will be by Sir Charles Waldstein, who will deal generally with the subject of "Industrial Art"; the third by Mr. Joseph Pennell on "Artistic Lithography." The subject of the fourth course will be announced later. The last will be by Mr. William Burton on "Recent Developments in the Ceramic Industry." A course of lectures will also be delivered under the Cobb Trust, established from the surplus of funds subscribed for a memorial to Mr. Francis Cobb, who died in 1901. The lecturer will be Mr. Plunket Greene, and the subject of the lectures will be "The Singing of Songs, Old and New." A course of Juvenile Lectures to be delivered as usual during the Christmas holidays will be given by Mr. Howgrave Graham, and will deal in a popular way with the subject of "Wireless Telegraphy." They will be very fully illustrated.

MEETINGS FOR THE WEEK.

TUESDAY, 18th.—Chadwick Public Lectures, 5. (The University of London, South Kensington). "The Place of the Open-air School in Preventive Medicine," by Sir George Newman, M.D.

WEDNESDAY, 19th.—Microscopical, 8. "Shell Structure in the genus Lingula, Recent and Fossil," by F. W. Chapman. "Development of an Embiid," by J. C. Kershaw.

THURSDAY, 20th.—Royal Society. "Neuro-muscular Structures in the Heart," by A. F. S. Kent. "Alleged Excretion of Creatine in Carbohydrate Starvation," by G. Graham and E. P. Poulton. "On *Medullosa Pusilla*," by D. H. Scott. "Origin and Destiny of Cholesterol in the Animal Organism—Part XI., The Cholesterol Content of Growing Chickens under different Diets," by J. A. Gardner and P. E. Lander. "Contributions to the Biochemistry of Growth—On the Lipoids of Transplantable Tumours of the Mouse and the Rat," by W. E. Bullock and W. Cramer.

— Chemical Society, 8.30. "Interaction of Sodium Amalgam and Water," by H. B. Baker and L. H. Parker. "Action of Variously Treated Waters on Sodium Amalgam," by L. H. Parker. "Some Derivatives of Oleanol," by F. Tutin and W. J. S. Naunton. "Some Derivatives of Phorone," by F. Francis and F. G. Willson. "Porosity of Iron," by W. H. Perkin. "Bleaching Action of Hypochlorite Solutions," by S. H. Higgins.

THE CHEMICAL NEWS.

VOL. CVIII., No. 2817.

SOME CURIOUS ATOMIC WEIGHT RELATIONS.

(A SUPPLEMENTARY NOTE).

By F. H. LORING.

THE report from France* (CHEM. NEWS, cviii., 322) that gallium is present in commercial aluminium may be of interest in connection with Sir J. J. Thomson's positive rays. Quoting from the *Roy. Soc. Proc.*, 1913, A, lxxxix. (Bakerian Lecture), Thomson says:—"On the plate on which the helium line was strongest—the salt was KI—I could see a very faint line correspoding to an atomic weight 35 or thereabouts. I should have thought this was due to a trace of chloride among the potassium iodide, except for the fact that when KCl was substituted for KI this line was not strengthened. I have not yet been able to get this line strong enough to measure it with sufficient accuracy to decide whether the particle producing it has an atomic weight exactly equal to the difference of the atomic weight of potassium and helium" (p. 19).

If gallium is widely distributed in nature, as indicated, its presence in a vacuum tube would not be strange. It has physical properties closely resembling mercury, and it might, if I interpret Sir J. J. Thomson's experiments aright, carry a double charge (compare mercury), and in consequence have an apparent atomic weight of half 70. Of course there might be an inactive gas of an atomic weight near to that of gallium (see *Phys. Zeit.*, 1911, xii., 111), but this possibility seems very remote.

Since gallium is in question here, it will be of some interest perhaps to consider its atomic weight. This element does not fall into line with the other elements in my scheme (CHEM. NEWS, 1909, xcix., 150), and, from the tabular arrangement given, it should apparently fall on the curve with bromine. This would entail a value of 71·37, which would find a place in a further extension of the scheme cited (see CHEM. NEWS, c., 281), and this value (taken as 71·33) together with the fact that the element in question is allied to thallium, renders possible the following series:—

Atomic weights.	Differences.	
H = 1·01*		
	7·89	
Be = 8·90		18·66 (*b*)
	26·55	
Cl = 35·45		9·33 (*a*)
	35·88	
Ga = 71·33		

$$2a = b;\ a+b = 28.$$

* Rounded to second decimal place, the true value being close to 1·008.

It will be seen that the atomic weight of beryllium is altered slightly, and hydrogen is assumed to be sufficiently related to helium to occupy a place at the head of a series (see CHEM. NEWS, 1912, cvi., 37). In passing upwards through a Mendeleeff group to the initial member, the continuity in properties ceases, in a sense, at the first element, yet a continuation is possible with a minimum change in some properties down the *next* group, thus linking up, for example, helium with hydrogen or lithium, or group O with group I. Wrapping the Table round a cylinder, group O may be represented as group IX. In regard to beryllium, quoting from Browning ("Introduction to the Rarer Elements," 1912, p. 20):—"The compounds of beryllium closely resemble those of aluminium." The significance of these relations will be seen upon a comparative study of this series with those previously given (CHEM. NEWS, 1913, cviii., 95, 188).

The atomic weight of gallium was determined by its discoverer, Lecoq de Boisbaudran, in 1878, and it would appear that no further determination has been made. It seems reasonable, therefore, not to attach too much importance to the early measurement, especially as a comparatively recent determination of the atomic weight of mercury has yielded a value 6/10ths of a unit higher than the previously accepted figure.

If active hydrogen is eligible as an initial member in a quaternian series, then nitrogen should also be eligible. Taking N = 14·00, Cr = 52·02, Ru = 101·70, and Gd 157·21, a fairly satisfactory series may be constructed, especially when it is noted that europium from spectroscopic considerations falls between cadmium and mercury. (Dr. W. M. Hicks in "A Critical Study of Spectral Series" says: —"An attempt is made to arrange the S and D series for europium and radium. Eu is found to fit the gap between Cd and Hg and a density 12·58 deduced for it," *Phil. Trans. Roy. Soc.*, 1912, ccxii., 33). Gadolinium, which is the next element, should then fall between indium and thallium. These elements were so placed in an alternative form of Periodic Table published in the CHEMICAL NEWS, 1909, c., 283.

The place assigned to ruthenium seems to imply a connection with the halogens, or group VII. This is brought out in my book "Studies in Valency," 1913, though the gradient is steep, if I may so express the transition in properties of the end members taken in what might, for convenience, be termed *vertical comparison* (see Table on page 23, and comments thereon).

There appear to be seven series (some are doubtful, however) of practically four members each, which I have termed *quaternian series*. In studying the typical valency values, when all the series are so arranged or grouped that the third element in each set is progressively higher in atomic weight than its predecessor of a previous set, the total valencies or group numbers per set increase progressively down the whole series, but Ni, Fe, and Co seem to require to be assigned to the VIth group, whilst the inactive gases seem best represented as belonging to a IXth group, and hydrogen might have a group number of VII. or VIII. (see "Studies in Valency," pp. 27 and 28).

Hydrogen may be the only survivor of a series of elements perhaps differing very slightly in atomic weight. A similar idea was proposed by Palmer (see Tilden "The Elements," p. 93). This idea, moreover, is supported by the absence of eight to ten elements between hydrogen and beryllium, as indicated by the series given above, since there are ten or eleven active elements between beryllium and chlorine, and twelve between chlorine and gallium. This observation also portends that hydrogen may not be the proper member to select for the head of the series, though a better fitting one may now be extinct.

From the standpoint of radio-activity, these missing members may have been all taken up in some process of evolution, so that if the lower atomic weight elements were to disintegrate they might give back these elements. Against this idea, however, is one that hydrogen is the *alpha* and *omega* of such a hypothetical series, since, indeed, it is eligible for either end of a standard Periodic Table, according as its properties are selected for comparison with those of group I. or group VII. In other words, perhaps this series had a representation in some *urstoff*, which, "consisting of an infinite number of immeasurably small particles gradually accreting out of formless mist," gave birth to hydrogen, this being in reality Sir William Crookes's well-known conception of the "Genesis of the Elements," at least in part.

Notwithstanding these apparent regularities, beryllium and nitrogen still remain in some respects anomalous from the standpoint of my original scheme, as do some subsequent developments, so that these studies are punctuated with uncertain or discordant factors.

* Boulanger and Bardet, Academy of Sciences, Oct. 27, 1913.

A SIMPLE THERMO-REGULATOR.

By J. G. Boyd and H. M. Atkinson.

A stout test-tube about 6×¾ has a good wooden cork (rubber is attacked by toluene), through which passes a narrow bore glass tube, fitting by a rubber band into the narrow part of an ordinary filtering tube.

This has a double bored stopper with two right angled glass tubes, one reaching down inside to near the top of the narrow bore tube, and ground off like the stem of a funnel, but more acutely, with a piece of carborundum.

Fig. 1.—Diagram of Arrangement of T-pieces.

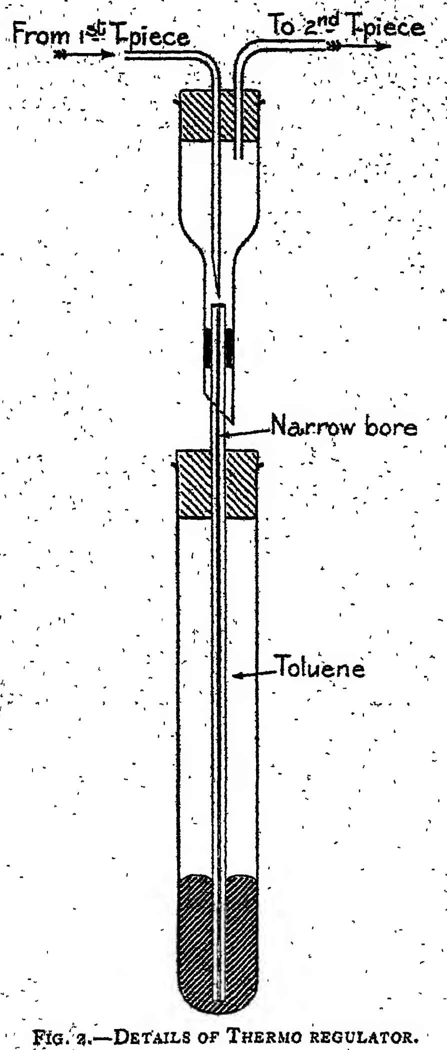


Fig. 2.—Details of Thermo regulator.

The other right angle tube extends to a little below the stopper. To fit, mercury is poured into the stout test-tube, the narrow bore dipping to bottom of this, then toluene or other liquid (water serves for approximations) to fill the test-tube, and tightly corked. To ensure that mercury fills the narrow bore tube this may be gently rotated a little way up before corking, and when corked pushed down again. A few drops of mercury into the filter tube to cover the top of the capillary, and the apparatus is ready to immerse in the thermostat. By raising or lowering the gas entry tube any desired volume of gas can pass through, and hence any desired temperature.

To prevent the flame of the Bunsen burner when very low from striking back we use two glass T-pieces to provide an independent gas supply to burner controlled by a screw clip.

Technical Institute, Limerick.

RAPID ESTIMATION OF MANGANESE, VANADIUM, AND TITANIUM IN PRESENCE OF ONE ANOTHER IN PIG-IRON AND STEEL.

By C. W. Wright.

The following method with care and skill is sufficiently accurate for most works purposes, but unless experience has been gained with synthetic solutions the results may be very wide of the truth.

The method is merely an extension of one given on p. 90 of "Analysis of Steel Works Materials" by Harry Brearley, on the volumetric estimation of vanadium. It is as follows:—

Dissolve 1·1 grm. in 35 cc. 1·2 nitric acid, filter off any graphite which may be present, keeping the bulk as low as possible. Add sodium bismuthate, and heat to destroy organic matter. Clear with sulphurous acid, and cool. When quite cold add an excess of bismuthate, pass through asbestos filter, wash with 3 per cent nitric acid water until clear. Add excess of N/10 ferrous sulphate, and then N/20 permanganate. So long as there is an excess of ferrous sulphate the permangate delivered at the rate of 2 or 3 drops per second disappears instantaneously, but immediately the oxidation of the vanadium commences there is a distinct retardation of the disappearing pink colour. It is almost instantaneous but quite recognisable with an experienced eye. The reading is now taken, and the titration finished to a permanent pink. In case of uncertainty the operation can be repeated any number of times by again adding ferrous sulphate and repeating the titration. From the above set of readings the vanadium and manganese can be calculated. The solution is now transferred to a comparison tube, hydrogen peroxide added, and then made up to a suitable volume not exceeding 100 cc. Meanwhile a similar steel or pig-iron which contains no Ti or V has reached a similar stage. To this is added an amount of vanadium solution exactly equivalent to that found in the sample. It is now only necessary,

Experiment	Iron present. Grms.	Per cent. Mn present.	Mn found.	V present.	V found.	Ti present.	Ti found
1.	1·1	0·33	0·32	Nil	Nil	Nil	Nil
2.	1·1	0·33	0·33	0·20	0·20	Nil	Nil
3.	1·1	0·33	0·34	0·20	0·20	Nil	Nil
4.	1·1	0·33	0·32	Nil	Nil	0·20	0·20
5.	1·1	0·33	0·33	Nil	Nil	0·20	0·20
6	1·1	0·33	0·34	0·10	0·11	0·20	0·19
7.	1·1	0·33	0·33	0·10	0·11	0·20	0·19
8.	1·1	0·33	0·34	0·20	0·20	0·20	0·20
9.	1·1	0·33	0·32	0·20	0·20	0·20	0·20
10.	1·1	0·33	0·33	0·09	0·10	0·21	0·20
11.	1·1	0·33	0·32	0·09	0·10	0·21	0·20

after addition of H_2O_2, to add standard titanium solution and compare. If the vanadium estimation is correct there should be no difficulty in comparing the colours developed. Any inaccuracy, however, will immediately declare itself by colours which will be difficult to compare. Both V and and Ti give highly coloured solutions on addition of H_2O_2, but as they are distinctly different in colour it is evident that the accuracy of the process depends on the skill and judgment exercised in determining the vanadium present. The accompanying figures show how near to the truth one can get.

THE PASSIVITY OF METALS.

By George Senter.

The phenomenon of passivity was discovered by Keir as far back as 1790 (*Phil. Trans.*, 1790, lxxx., 359). He observed that iron, after treatment with concentrated nitric acid, had lost the property of precipitating silver from solutions of silver salts, and was no longer attacked by dilute nitric acid. The name "passivity" we owe to Schönbein, who made many important contributions to our knowledge of the subject (*Pogg. Ann.*, 1836, xxxvii., 390; xxxviii., 444; xxxix., 342; 1837, xli., 53; 1838, xliii., 103). Faraday's name is also closely associated with the early history of this subject in connection with his well-known suggestion (*Phil. Mag.*, 1836, ix., 53) that passivity is due to the formation of a coating of oxide on the surface of the metal—an explanation which still has its supporters. For a number of years after 1840 our knowledge of passivity made comparatively little progress, but about fifteen years ago a new era of rapid advance set in. This stage was initiated by the classical experimental investigations of Hittorf, who worked chiefly with chromium (*Zeit. Phys. Chem.*, 1898, xxv., 729; 1899, xxx., 48; 1900, xxxiv., 385). Among recent investigators the names of Le Blanc, Foerster, Haber, G. C. Schmidt, and their co-workers deserve special mention. The predominant share which our German colleagues have taken in the recent developments of this subject is reflected in the number of papers which they have been good enough to contribute to our proceedings this evening.

As a general rule, progress in our knowledge of any particular subject is most rapid when there is considerable divergence of opinion with regard to the interpretation of the experimental results. Such divergence of opinion has been particularly marked in connection with passivity, and even at the present time three entirely different "explanations" of the phenomenon have their supporters. The controversy has now, however, reached such a stage that a considerable measure of agreement has been reached on many points, and it is hoped that the open discussion of the subject arranged by this Society, by emphasising points of agreement as well as points of difference, may indicate the most fruitful directions for further experimental investigation, and thus contribute in no small degree to progress in a very interesting and important subject.

History of the Subject.

Keir was led to the discovery of passivity by following out an observation of Bergmann that some samples of iron are capable, others incapable, of displacing silver from its salts. One of Keir's most important observations may fittingly be described in his own words:—"I digested a piece of fine silver in pure and pale nitrous [nitric] acid, and while the dissolution was going on and before the saturation was completed I poured a portion of the solution upon pieces of clean and newly scraped iron wire into a wine-glass and observed a sudden and copious precipitation of silver. The precipitate was at first black, then it assumed the appearance of silver, and was five to six times larger in diameter than the piece of iron wire which it enveloped. The action of the acid on the iron continued some little time and then it ceased, the silver redissolved, the liquor became clear, and the iron remained bright and undisturbed in the solution at the bottom of the wine-glass, where it continued during several weeks without suffering any change or effecting any precipitation of the silver."

Further experiments showed that the liquid had not lost its power of acting on *fresh* iron, although it had ceased to act on the piece exposed to it, so that the change was in the iron and not in the liquid. This led to the discovery that concentrated nitric acid alone renders iron passive, and it was further found that a sample of inactive iron regained its activity by rubbing it at a point or by bringing it in contact with a piece of active metal. The further remarkable observation was made that when a piece of active metal was placed in acid in which a piece of passive metal was lying, so that the two pieces did not touch, in a short time the passive metal became active. Keir, at the end of his paper, expresses his intention of returning to the subject in later communications, but this promise remained unfulfilled.

The next important contributor to this subject was Schönbein (*loc. cit.*). Space will only admit of a brief reference to two of his observations. In a letter to Faraday he points out that a piece of iron could be rendered passive by heating one end of it in an alcohol flame for a moment or two—not only the heated portion but the remainder of the wire is rendered passive. Further, other wires placed in contact with the partially oxidised wire are not affected in nitric acid of density 1·35 provided the oxidised end is first dipped in the acid; under ordinary conditions the wires dissolve readily in acid of this density. Later investigations appear to show that portions of wire in contact with the heated portion are not passive, but can be passivated more readily than ordinary iron (Hittorf, *Zeit. Phys. Chem.*, 1900, xxxiv., 395; Heathcote, *Ibid.*, 1901, xxxvii., 368). The contradictory results obtained with nitric acid are probably to be accounted for by the observation that under certain conditions a relately dilute acid (D = 1·250) can render iron passive (Heathcote, *loc. cit.*).

Schönbein was one of the earliest to investigate passivity by electrochemical methods, and he made the important discovery that iron could be rendered passive by making it an anode in a cell in which oxygen acids were subjected to electrolysis (so-called "anodic polarisation"). Schönbein did not himself suggest any explanation of passivity, but raised objections to the oxide theory when it was put forward by Faraday. The reasons given by Faraday in favour of his theory are as follows:—

1. All known passivity phenomena are oxidation processes.
2. Iron coated with oxide is insoluble in acids.
3. The passive condition readily disappears on polishing the metal.

His words are as follows (*cf.*, "Experimental Researches," Everyman's Library edition, p. 326):—"The iron is, in fact, as if it had no attraction for oxygen, and therefore could not act on the electrolyte present, and consequently could produce no current. My strong impression is that the surface of the iron is oxidised or the superficial particles of the metal are in such relation to the oxygen of the electrolyte as to be equivalent to an oxidation."

Schönbein urged, among other objections to Faraday's theory, that iron rendered passive in acids showed no trace of a coating of oxide. To this Faraday answered that he could find no better explanation, and that he would not maintain that the coating consisted of one of the known oxides, but resembled more a condition of very fine equilibrium.

As already mentioned, Faraday's explanation of passivity was pretty generally accepted up to the commence-

* General Introduction to the Discussion on "The Passivity of Metals" held before the Faraday Society, November 12, 1913.

ment of Hittorf's investigations in 1898. The bearing of these important investigations on the nature of passivity is dealt with below. Hittorf pointed out many serious objections to the oxide theory, but did not himself put forward any very definite explanation of passivity phenomena. In connection with his observation that active chromium dissolves in the divalent form whilst passive chromium dissolves at a much more higher potential with formation of compounds containing sexavalent chromium, it has been suggested that the passive form of a metal is a different allotropic modification, much "nobler" than the active form (see below).

A third theory of passivity, the so-called "reaction velocity theory," was put forward by Le Blanc in 1900 (*Zeit. Elektrochem.*, 1900, vi., 472; 1905, xi., 9; *Boltzmann Festschrift*, 1904, p. 183), and has exercised a profound influence on the recent development of the subject. These three theories of passivity are discussed, and the arguments for and against them briefly stated in the next section.

Theories of Passivity.

The more important phenomena which have to be accounted for on any theory of passivity are as follows. The passive state is best known in connection with iron, cobalt, and nickel, but most if not all the metals may be made to assume this state under suitable conditions. Passivity may be induced by immersing the metal in an oxidising agent such as nitric or chromic acid, and in solutions of alkali hydroxides; also by anodic polarisation in a great variety of electrolytes. When the force producing passivity is removed the metal as a rule returns to the active state, slowly at first and then more rapidly, in some cases almost instantaneously. When the surface of a metal in the passive condition is scratched or rubbed, it regains its activity at once. Treatment with acids, cathodic polarisation with hydrogen, and raising the temperature all favour return to the active condition. A metal becomes much more positive (more "noble") when it changes from the active to the passive condition, and does not dissolve when the equilibrium potential is reached. On further increasing the anodic potential the metal may dissolve as a more highly oxidising ion (*e.g.*, chromium), or the current may be employed mainly or entirely in discharging anions. The rise of potential on anodic polarisation is usually slow at first, and then there is a sudden rise of considerable amount, the metal becoming almost insoluble. The nature of the anion has considerable influence. Thus the ions of oxidising acids, such as NO_3 and ClO_3' favour passivity, whilst Cl' and Br' have the contrary effect. Other phenomena met with in this connection will be mentioned in the course of the discussion of the different theories of passivity.

As already mentioned, three theories of passivity have obtained a greater or less degree of recognition:—

1. The oxide-film theory of Faraday, already referred to.
2. The valency theory of Krüger-Finkelstein (*Zeit. Phys. Chem.*, 1902, xxxix., 104) and W. J. Müller (*Ibid.*, 1904, xlviii., 577); according to this theory passivity phenomena are due to the change of a metal to the "nobler" modification.
3. The reaction velocity theory of Le Blanc (*loc. cit.*). In its most general form this theory states that passivity phenomena are due to slow rate of change (electrochemical or purely chemical) at the anode. In this form the reaction velocity theory is little more than a statement of the facts, and several special hypotheses have been put forward as regards the mechanism of the retardation. Thus we have—

(*a*) *The oxygen charge hypothesis* of Fredenhagen (*Zeit. Phys. Chem.*, 1903, xliii., 1; 1908, lxiii., 1) and Muthmann and Frauenberger (*Sitzungsber. der Kgl. Bayrischen Akad.*, 1904, xxxiv., 201). The cause of passivity is to be sought in the slow rate of reaction between the anode and the oxygen liberated there, with the result that the anode becomes charged with the gas, or, alternatively, a metal-oxygen alloy is formed.

(*b*) *The anion discharge hypothesis*, according to which the main change at the anode is not the formation of metal ions but the discharge of anions; the slow reaction of the discharged anions with the metal produces passivity. The views of Sackur (see below) are based on the assumption of a primary anion discharge.

(*c*) *The hydrogen activation hypothesis* of Foerster (*Abhandlungen der Bunsen Gesellschaft*, 1909, No. 2) and of Schmidt (*Zeit. Phys. Chem.*, 1911, lxxvii., 513), according to which the normal condition of iron is passive and it only becomes active under the influence of a catalyst. According to Foerster the catalyst is hydrogen; according to Grave (*Zeit. Phys. Chem.*, 1911, lxxvii., 513), a pupil of Schmidt, it is hydrogen ions.

(*d*) *The retarded ion hydration hypothesis* of Le Blanc ("Lehrbuch der Elektrochemie," 5th edition, p. 285).

Each of these theories will now be briefly considered.

The Oxide Film Theory.

The mode of action of a film of oxide or other insoluble substance in causing passivity is presumably that it coats the electrode and mechanically hinders metallic ions from entering the solution. Current can only pass when the anode potential is increased to such an extent that anions are discharged.

There can be no doubt that passivity is in some cases due to the formation of an insoluble coating. Thus when lead is anodically polarised in sulphuric acid a coating of lead sulphate forms on the anode and protects the metal against further action. It may be, however, as has been suggested by supporters of other theories of passivity (Foerster, *loc. cit.*), that such films are in some cases at least a consequence rather than a cause of passivity.

An important investigation which is often cited in favour of the oxide theory is that of E. Müller and Spitzer (*Zeit. Anorg. Chem.*, 1906, l., 321), who found that on anodic polarisation in alkali, iron, cobalt, and nickel became coated with the respective oxides and simultaneously became passive. In order to meet the objection that this might be a secondary phenomenon, they avoided the presence of the metals altogether by examining the behaviour of platinum electrodes coated with the oxides of iron, cobalt, and nickel respectively. Such electrodes on anodic polarisation in sodium hydroxide were found to behave in the same way as passive electrodes of the metals themselves, from which the conclusion was drawn that the behaviour of the latter is also due to a coating of oxide.

Haber and Goldschmidt (*Zeit. Elektrochem.*, 1906, xii., 49) cite in favour of the oxide theory the observation that iron which has been rendered passive by anodic polarisation in alkaline solution without losing its metallic lustre becomes coated with a layer of hydroxide on addition of halogen ions. Le Blanc has made similar observations with nickel anodes, but interprets them in an entirely different way. Haber and Maitland (*Ibid.*, 1907, xiii., 309) have shown that in contrast to the behaviour of alkali of moderate concentration very concentrated alkali renders iron active and that it acts by dissolving a superficial film of oxide.

The behaviour of iron electrodes on anodic polarisation has yielded results which have been adduced, more particularly by P. Krassa, in support of the oxide theory (*Zeit. Elektrochem.*, 1909, xv., 490). It is well known that iron readily becomes passive by anodic polarisation in relatively dilute alkali. Krassa now shows that in boiling concentrated alkali iron can be anodically polarised for some time without losing its activity when the current density is not too large; on continuing the polarisation the anode slowly becomes passive, but great stress is laid upon the fact that the formation of a visible coating precedes passivity. With high current density the anode at once becomes passive.

More recently Grube (*Zeit. Elektrochem.*, 1912, xviii., 189), who has made a careful investigation of the electro-

lytic oxidation of ferrocyanides, has shown that anodes of iron, nickel, cobalt, copper, lead, and silver in neutral solution of potassium ferro- and ferri-cyanide and anodes of iron, lead, silver, and zinc in alkaline solutions of the same salts, become strongly passive, and in all cases this is ascribed to the formation of an insoluble coating on the anode. In other cases there is no evidence of an insoluble coating and the passivity is ascribed to an oxygen charge which retards the liberation of cations of the metal.

The weak point in all these investigations is that they were carried out only in neutral or alkaline solution, and therefore cannot afford an explanation of passivity in general, especially in acid solution.

Objections to the Oxide Theory of Passivity.—Very serious objections to the oxide-film theory as an explanation of passivity in general have been adduced by Hittorf, Le Blanc, Fredenhagen, Foerster, and others. These will now be briefly considered.

Hittorf maintains that if the passivity of iron and chromium is to be ascribed to a coating of oxide, such oxides have not so far been discovered, since none of the known oxides possess the necessary properties. The effect of rise of temperature in destroying passivity is very difficult to account for on the oxide theory. Hittorf's so-called "experimentum crucis," whereby chromium, which was capable of decomposing hydriodic acid with the formation of the iodide and liberation of hydrogen, was rendered passive by anodic polarisation in a solution of the same acid in the absence of oxygen, is also impossible to reconcile with the oxide theory.

Finkelstein (*loc. cit.*) has shown by means of polarisation capacity measurements on passive iron that if there is a coating of oxide it must conduct electricity like a metal. He further points out that the assumption of the formation of a definite oxide is difficult to reconcile with the fact that on anodic polarisation a metal may take all intermediate potentials from the active to the passive condition. The latter objection is perhaps met to some extent by Haber's discovery that oxide films, in some cases at least, are porous, so that the mechanical hindrance to the escape of metallic ions would presumably increase with the thickness of the coating. A somewhat similar objection was advanced by Fredenhagen (*loc. cit.*), who applied a gradually increasing or a gradually diminishing e.m.f. to iron, nickel, or chromium electrodes immersed in sulphuric acid, and measured the p.d. at the electrodes and the strength of the polarising current. It was found that when the anode was slowly polarised the potential gradually became nobler, and then there was a rapid change to the passive condition. Conversely, when the electrode was allowed to recover its activity the potential fell gradually at first, and then there was a sudden transformation to the completely active condition. There was, however, no evidence of a definite activity or passivity potential, since the results depended on the concentration of the acid and other factors. These facts are very difficult to reconcile with the assumption that passivity is due to the formation of a definite oxide.

The most serious objection to the oxide-film theory, however, is based on measurements of the reflecting power of metallic surfaces. Müller and Koenigsberger (*Zeit. Elektrochem.*, 1907, xiii., 659) state that they are able to measure differences of 0·5 per cent in the reflecting power of two metallic surfaces, and in this way have detected the presence of oxide films of molecular dimensions (0·8 $\mu\mu$ in the case of lead peroxide). Two iron electrodes which had been polarised for some time by generating hydrogen and oxygen respectively in contact with them were found to show no difference whatever in reflecting power, although one was active and the other passive. The objection raised by Haber and Goldschmidt and by Krassa, that cathodic polarisation with rapid evolution of hydrogen had not reduced the oxide on the surface, and therefore that in both cases the reflecting power of oxidised films was being compared, does not seem very convincing.

The general impression gained by a review of the evidence is that although the oxide-film theory may apply in certain cases, especially to electrodes anodically polarised in alkaline solution, it can no longer be regarded as a satisfactory explanation of passivity in general.

The Valency Theory of Passivity.

This theory, first brought forward by Finkelstein (*loc. cit.*), is based on the assumption, due to Krüger (*loc. cit.*), that the modifications of a metal with different valencies are all present in the solid metal in proportions depending on the temperature and other factors, and that the electrochemical behaviour of metals depends on the relative concentrations of these modifications. W. J. Müller (*Zeit. Elektrochem.*, 1904, x., 832) has attempted to find support for this theory from considerations based on the electron theory of conductivity in metals. Both Krüger and Finkelstein recognise, however, that this theory affords no satisfactory explanation of *sudden* changes from the passive to the active condition, nor of the marked effect of the nature of the anion on passivity phenomena. The main point of the valency theory is that the cause of passivity is to be sought in the metals themselves, an assumption which is incompatible with the specific effect of the anions just referred to. The valency theory has met with very little support during the last four or five years, and therefore need not be further considered here.

The Reaction Velocity Theory.

As already mentioned the reaction velocity theory of passivity was first put forward by Le Blanc. One way of stating this theory is that metals in the passive condition send their ions of lowest valency only very slowly into solution. Thus in the case of iron the change represented by the equation $Fe + 2F \rightarrow Fe^{\cdot\cdot}$ proceeds very slowly when the metal is in the passive condition. This is not to be interpreted in the sense that the actual taking up of electric charges is a slow process (on the contrary, purely ionic reactions are practically instantaneous), but it is assumed that the ionisation of the metal is associated with *chemical* changes, and when these changes are very slow, passivity phenomena occur (compare Foerster, *loc. cit.*, p. 23). In its general form the reaction velocity theory is little more than a statement of the facts, and attention is mainly directed to the exact nature of the chemical changes associated with the purely electrical changes.

As already mentioned, there are at least four hypotheses as regards the nature of these chemical changes: (*a*) The oxygen charge hypothesis; (*b*) the anion discharge hypothesis; (*c*) the hydrogen activation hypothesis; (*d*) the retarded ion hydration hypothesis.

The Oxygen Charge Hypothesis.—Two or three years after the appearance of Le Blanc's paper on the subject, Fredenhagen (*loc. cit.*) put forward the view that passivity is due to the accumulation of a charge of gaseous oxygen on the metal, the slow reaction being that between metal and oxygen. Sudden changes from the active to the passive condition and *vice versa*, which sometimes occur, are ascribed to the transition from a non-homogeneous state of polarisation into a continuous gas charge covering the electrode uniformly. Even in the latter condition the electrode is not completely inactive, as a slow reaction takes place between it and oxygen.

There is no doubt that the oxygen charge theory represents a considerable advance on the oxide-film theory, since (1) it accounts for the effect of rise of temperature in removing activity; (2) it is not inconsistent with the results of optical measurements, since gas charges do not alter the reflecting power of metallic surfaces; (3) it is also, as an irreversible reaction, compatible with Fredenhagen's observation (*ante*) that the curve of gradually increasing activity does not correspond with that of gradually increasing passivity.

There are, however, formidable objections to the oxygen charge theory, of which the following may be mentioned:—

1. It does not account for Hittorf's "experimentum crucis" on the passivity of chromium in hydriodic acid (see above).

2. Certain metals which can be rendered passive combine readily with oxygen under other circumstances, and no explanation is afforded of their assumed inactivity towards this gas when in the passive state.

3. It does not account for the fact recently established by Grave (*loc. cit.*), that iron becomes passive on heating in nitrogen.

4. It affords no explanation of the passivating effect of alkalis on iron.

For these reasons the oxygen charge theory cannot be regarded as affording a satisfactory explanation of passivity phenomena.

The hypothesis of primary anodic discharge, first put forward by O. Sackur (*Zeit. Elektrochem.*, 1908, xiv., 612), promises to play a considerable part in the future development of electrochemistry. It has been generally assumed that when a metal dissolves at the anode, the primary process consists in a passage of the metal into solution in the form of ions. Sackur put forward his hypothesis of primary anion discharge without much experimental proof; for some time it met with little acceptance. Recently, however, support has been lent to this hypothesis by the observation of Haber and Zawadzki (*Zeit. Phys. Chem.*, 1911, xviii., 228) that when solid compressed silver salts are electrolysed between electrodes of silver considerable polarisation occurs, and this polarisation is greatly increased by lowering the temperature. The probable explanation is that the transport of the current from solid electrolyte to anode is effected by the passage of negative electrons from anions to metal; the discharged anions then attack the silver anode, the latter change being greatly retarded by cooling. It is not improbable that the mechanism of current transport is the same in aqueous solution, but in this case the discharged ion in presence of the solvent reacts rapidly with the electrode, so that little or no polarisation occurs.

It is evident that the above considerations afford an explanation of passivity phenomena on the basis of the reaction velocity theory. Sackur's explanation is rather complicated. He assumes that every electrode contains a certain amount of dissolved hydrogen formed by interaction with $H^{\cdot}$ ions in the electrolyte; the hydrogen concentration corresponds to the equilibrium represented by the equation (for a bivalent metal)—$Me + 2H^{\cdot} \rightleftharpoons H_2 + Me^{\cdot\cdot}$. The discharged anion (oxygen, halogen, &c.) reacts with and removes the hydrogen. To re-establish equilibrium the above reaction then proceeds in the direction of the upper arrow, so that the anodic dissolution of metals is a chemical process. Passivity is brought about by a slow rate of reaction between the hydrogen and the discharged anion, so that the latter (oxygen, &c.) accumulates on the electrode. There is considerable resemblance as regards the final stage between this hypothesis and the gas charge hypothesis. Although the above hypothesis is very suggestive, it is in one respect self-contradictory, as has been pointed out by Auerbach (*Zeit. Elektrochem.*). It starts with the assumption that the metals do not primarily ionise, whereas the assumed interaction of the metal with hydrogen is just such an ionisation.

The hydrogen activation hypothesis, based on the assumption that the *pure* metal is passive and only becomes active under the influence of a catalyst, was put forward by Foerster (*loc. cit.*) on the basis of a very detailed investigation of the electromotive behaviour of iron. If the reaction velocity theory, that passivity is due to the slow rate of ionisation of the metal, is correct, then since the reaction $Fe + 2F \rightleftharpoons Fe^{\cdot\cdot}$ is reversible, the converse process, the electrolytic precipitation of iron, will probably also be a retarded reaction, a deduction which is fully confirmed by experiment.

Foerster points out that the hydrogen activation theory is in agreement with the effect of cathodic polarisation and of acids in promoting activity, also with the behaviour of iron in air, under the influence of oxidising agents, in the presence of alkali, &c. He does not deny that oxide films may play a part in passivity phenomena in certain cases, but considers that the production of such films is a consequence rather than a cause of passivity. In the case of anodic polarisation of iron in alkali, for instance, the underlying cause of passivity is the absence or removal of hydrogen, and the deposition of an oxide follows on account of the inactive condition of the metal. The chief advantage of this theory over the oxide theory is that it is valid both for polarisation in acid and alkaline solution. It is pointed out that other substances than hydrogen may facilitate the reaction $Fe + 2F \rightarrow 2Fe$; for instance, the presence in solution of substances capable of taking up negative or giving up positive charges, such as the halogens or metallic ions of higher valency, *e.g.*, $Fe^{\cdot\cdot\cdot}$. It is well known that the dissolution of passive metals is greatly facilitated by the presence of such substances.

Strong support has been given to Foerster's hypothesis by E. Grave (E. Grave, (*Zeit. Phys. Chem.*, 1911, lxxvii., 513), who, however, contends that the catalyst is not hydrogen, or an alloy of hydrogen with the metal, as Foerster assumes, but hydrogen ions. In favour of this view the following facts are adduced. Iron and nickel become active when heated in hydrogen, but become passive when strongly heated in air, nitrogen, or a vacuum. Molecular hydrogen, after being in contact with iron and nickel, does not alter the potential, but ionised hydrogen renders the metals active, and iodised nitrogen renders them passive. Hydrogen ions are given off when a metal changes from the active to the passive state. When iron is saturated with $H^{\cdot}$ ions, the charge given off on heating is greatly increased. When iron is rendered active at one point by bringing it in contact with hydrogen ions, other parts of the metal are rendered active by diffusion. This explanation of passivity has also been shown to afford an explanation of the well-known periodic phenomena at electrodes of chromium and other metals which can be rendered passive (A. Adler, *Zeit. Phys. Chem.*, 1912, lxxx., 385).

Quite recently, Flade and Koch (*Zeit. Elektrochem.*, 1912, xviii., 335) have attempted to decide between the oxygen and hydrogen theories of passivity as follows:—If an active electrode is heated and means are taken to remove any hydrogen given off, the metal must become passive if the hydrogen theory is correct, and active if the oxygen theory is valid. Further, if passive iron is heated in a vessel containing a reducing gas which is neither hydrogen nor a compound containing hydrogen, the metal must remain passive if the hydrogen hypothesis applies, and must become active if the oxygen hypothesis is valid. It was found that an active iron electrode remained active on heating in a vacuum, which speaks in favour of the oxygen theory. On the other hand, iron which had become passive by standing in air remained passive when heated in carbon monoxide, which appears to be contrary to the oxygen theory. It was found, however, that heating in carbon monoxide also renders active iron passive, and the author maintains that the result of the second experiment is also compatible with the oxide theory. With reference to the first experiment, the possibility of an objection to the effect that the metal after heating in a vacuum may still contain traces of hydrogen is foreseen, but is not regarded as valid.

Le Blanc's Views.—As Le Blanc was the first to put forward the reaction velocity theory of passivity, his views on the later developments of the subject are naturally of interest. I cite them according to the latest edition of his "Lehrbuch der Elektrochemie" (fifth edition, p. 283). Foerster's suggestion that pure iron is the passive form and that it only becomes active in the presence of a catalyst is apparently not accepted. It is assumed that active iron sends out ions into the electrolyte, and that in the case of metals which tend to become passive these ions only combine very slowly with water, according to the

equation Ion + water $\rightleftarrows$ ion hydrate. On this account the concentration of free ions at the electrode becomes so great, and therefore the potential difference between electrode and solution becomes so considerable, that the discharge of anions or of oxygen begins. This hypothesis of passivity is based on the observation that even when the ion concentration at the electrode is sufficiently large, polarisation occurs both at anode and cathode in many cases where it was not previously suspected (Le Blanc, *Abhandlungen der Bunsen Gesellschaft*, No. 3, 1910). In order to explain these facts a difference between free and hydrated ions is postulated, and it is assumed that the hydration and dehydration of ions is under certain circumstances a relatively slow process. It should be mentioned that this assumption is due in the first instance to Foerster and Luther (Foerster, *loc. cit.*, p. 55), and was applied by Foerster to account for the retardation observed in the discharge of Fe·· ions at an iron kathode. It may further be added that although the view that ions are more or less hydrated has met with wide acceptance, there does not appear to be any independent evidence of the slow hydration which forms the basis of Le Blanc's theory of passivity.

Conclusion.

The more important phenomena of passivity have now been briefly discussed, and the chief theories which have been put forward to explain these phenomena have been described. The main object of this paper is to afford a résumé of the present position of the subject, and it would be out of place in opening the discussion to attempt any detailed comparison of the relative merits of the different theories. This can be more profitably attempted when the various contributions to the discussion are available.

In all probability it will eventually be found that no one theory will serve to account for all the phenomena of passivity. Thus both Le Blanc and Foerster, although in the main favouring other explanations, recognise that the formation of insoluble films on the electrodes plays a part in some cases of passivity. The hydrogen activation theory, which is perhaps most in favour at the moment, is undoubtedly valid to some extent, as the effect of nascent hydrogen in restoring the activity of passive metals is beyond dispute. (According to Hittorf and Grave *molecular* hydrogen does not restore the activity of passive metals.) Whether iron entirely free from hydrogen is necessarily passive, as Foerster and Schmidt assume, would, however, appear to be still open to discussion. In particular, the activating influence of the free halogens (*e.g.*, iodine in potassium iodide) is difficult to reconcile with this view, as it would appear that the metal in the absence of hydrogen is capable under these circumstances of sending charged ions freely into solution, which is contrary to the theory. On the other hand, it should not be difficult to devise a plausible explanation of the *sudden* changes from the active to the passive state and *vice versa* on the basis of the hydrogen activation theory, whereas these changes are difficult to reconcile with any of the other theories. It is not easy to understand, for instance, how such sudden changes could occur on the basis of the ion hydration hypothesis favoured by Le Blanc.

Decomposition of Decahydroquinoline into Optical Isomers.—Bruno Veneziani.—The structural formula of decahydroquinoline is analogous to that of decahydronaphthol, each substance possessing two central carbon atoms and being asymmetrical. Decahydroquinoline being strongly basic can readily be split up into the two optical isomers by adding the calculated quantity of *d*-bromocamphosulphonic acid and subjecting to fractional crystallisation. The bromocamphosulphonate of the *d*-isomer is much the less soluble in water. The rotatory powers are as follows :—*d*-Decahydroquinoline, $[\alpha]_D = +1\cdot28$; *l*-decahydroquinoline, $[\alpha]_D = -1\cdot02$.—*Atti della Reale Accad. dei Lincei*, 1913, xxii. [ii.], No. 4.

RECENT WORK IN INORGANIC CHEMISTRY.*

By JAMES LEWIS HOWE.

(Concluded from p. 239).

Complex Compounds.—Perhaps the most important work in inorganic chemistry during the past year has been that of Werner in his development of inorganic stereoisomerism and optical isomerism, especially in the complex compounds of cobalt. In the *Annalen* (ccclxxxvi., 1) he gives a complete review of his work on the stereoisomerism of cobalt compounds, much of which has been published from time to time in the *Berichte*. A few points in this work may be noted. Diethylenediamine compounds having different radicles in the other two places within the co-ordinated group as $\left({}^{A}_{B}\text{Co}\ en_2\right).C$, give rise to what Werner calls ionisation-metamerism, and furnish three isomers, according as the negative ion is A, B, or C. In addition each of these isomers may exist in both *cis* and *trans* form, according as A and B (or B and C, or A and C) are on contiguous or opposite corners of the fundamental octahedron of the co-ordinated group. Thus there are six possible isomers, and in the case where A, B, and C represent NO_2, Cl, and SCN, all six have actually been prepared. Some considerable progress has been made toward the systematisation of the properties of these compounds. For example, *cis* compounds generally are more soluble than the *trans* isomers, as is true of organic compounds; the colour of a compound is far more influenced by an element or group within the co-ordinated radical than by one outside; the order in which different groups within the radical affect the colour is the following, the first named having least effect:—CN, CO; NO_2, *en*, NH_3, NCS; SO_3; OH_2, O.NO, O.Acyl, OH; Cl, Br, I. In various intramolecular reactions transformation of isomers often occurs, but the direct transformation of stereoisomers into each other is rare, and probably results only from the formation of intermediate products. Three types of these reactions in which rearrangement may take place are noticed:—One (Einlagerungsreaktion), in which NH_3 or H_2O enters the complex radical, forcing the ionisation of group or atom of the complex, as—

$$\left({}^{SCN}_{Br}\text{Co}\ en_2\right).Br + NH_3 = \left({}^{SCN}_{H_3N}\text{Co}\ en_2\right).Br_2;$$

one (Verdrängungsreaktion), where NH_3 or H_2O passes out of the complex an atom or group outside the radical taking its place, as—

$$\left({}^{H_3N}_{Cl}\text{Co}\ en_2\right).(NO_2)_2 = NH_3 + \left({}^{O_2N}_{Cl}\text{Co}\ en_2\right).NO_2;$$

and a third (Substitutionsreaktion), where one negative atom or group is replaced by another. Inasmuch as the ordinary conception of replacement of atoms or groups, according to which an atom passes out of the group and the substituting atom takes its place, is inadequate to account for the stereometric changes which occur, Werner suggests a new theory. Every atom or group in the second sphere of a complex salt, that is outside the co-ordinated group, is attracted by the central cobalt atom, which seeks to draw the outside atom into the co-ordinated group. The *direction* of this attraction will depend upon the constitution of the complex; at all events this attraction will be stronger in some directions than in others. This will determine in what position the atom (or group) will enter the complex. On its entrance, the cobalt atom having but six co-ordination valencies, some other atom (or group) must leave the complex, and it will be the one for which the cobalt atom has (under the circumstances) the least attraction, and it may or may not be the atom which previously occupied the place where the newly entering atom has entered. Re-arrangements are thus not anomalous, but are founded on the ordinary course of the

* *Journal of the American Chemical Society*, xxxv., No. 2.

reaction. Werner suggests that the same idea is applicable to organic chemistry, where such transformations are by no means infrequent, and in particular calls attention to its applicability to the Walden re-arrangement.

One other class of products must be noted, which are formed by direct addition to groups within the co-ordinated complex. Such, for example, is the addition of a silver atom to the isothiocyanate group:—

$$\left(\begin{matrix}SCN\\H_3N\end{matrix}Co\ en_2\right).S_2O_6+AgNO_3=\left(\begin{matrix}AgSCN\\H_3N\end{matrix}Co\ en_2\right)\begin{matrix}NO_3\\S_2O_6\end{matrix}$$

In such cases frequently the silver atom is not removed on treatment with HCl. This type of reaction is also exemplified by Kirmreuther's sulphaminic acid derivatives of the chloroplatinites described last year.

Werner has also developed the work begun the previous year on the optical isomerism of the cobalt complex (*Ber.*, xliv., 3272, 3279; xlv., 121, 3281, 3287, 3294). Numerous compounds of the types $\left(\begin{matrix}A\\B\end{matrix}Co\ en_2\right)$ and $\left(\begin{matrix}A\\A\end{matrix}Co\ en_2\right)$ have been prepared, and the racemic form split into the optical isomers, most frequently by the use of the bromocamphorsulphonates. In many cases it is possible to go from one compound to another without changing the character of the activity. The phenomenon of mutarotation sometimes appears; the chloronitro-compound increases from a rotation of $[\alpha]_D=20°$ to a final constant of 52°. In other cases, as with the chlorobromo-compounds, the rotation decreases rapidly, and within an hour all activity has disappeared. Complexes were also prepared in which A and B in the above formulæ are represented by a single bivalent group, as carbonate and oxalate. The two compounds showed an opposite activity from that of the dichloro compounds from which they were derived, the lævo-dichloro-compound giving a dextro-carbonato- and dextro-oxalato salt. The carbonato salts have a high rotation, that of the chloride, $(CO_3Co\ en_2).Cl$ being $[\alpha]_D=\pm 350°$, while the carbonatodithionate is $[\alpha]_D=\pm 216°$, a much greater difference than is usual for different salts of the same complex. While the carbonato salts go slowly over into the racemic form the oxalato salts retain their activity even on boiling. Perhaps the most remarkable case of isomerism is that of the triethylenediamine compounds (Co en_3), where there are three identical bivalent groups in the complex, but which should exist in two non-superposable forms. Here the bromocamphorsulphonates gave no assistance in resolving the isomers, but by adding sufficient silver tartrate to precipitate two of the three atoms of chlorine in $(Co\ en_3).Cl_3$, the dextrochlorotartrate crystallised out, and the lævo salt formed was recoverable from the mother-liquor. From these salts both forms of optically active chlorides, bromides, and nitrates were formed. The corresponding triethylenediamine chromium racemates could not be resolved by tartrates nor by bromocamphorsulphonates, but by using nitrocamphor this was accomplished (*Ber.*, xlv., 865). The rotation of the optical isomers of these chromium salts was less than that of the cobalt salts, confirming what had already been found regarding the dichloro-diethylenediamine salts of these two metals. A further development of this work on inorganic optical isomerism is the preparation by Werner (*Ibid.*, p. 1228) of the optical isomers of triethylenediamine rhodium salts. Here the racemates could be split both by the tartrate and the nitrocamphor method, and the isomers showed decided stability, it being possible to evaporate the solutions without decreasing their optical activity. How much the nature of this activity depends upon the special nature of the central atom is shown by the fact that while the rotation of the rhodium compounds is quite similar in amount to that of the corresponding chromium compounds, it is opposite in sign, those rhodium salts having the same composition and configuration as the dextro-chromium salts, being lævorotary. Werner was also able to prepare (*Ibid.*, p. 433) by the tartrate method the lævorotatory form of tri-*αα*-dipyridyl iron chloride, bromide, and iodide. The rotation is very high (in the neighbourhood of 500°), but falls rapidly owing to formation of the racemate. It thus appears that inorganic optical isomerism is not confined to ethylenediamine compounds, nor to the compounds of trivalent metals, since the iron in the pyridyl compound is bivalent. It should, however, be noted that in spite of the most brilliant confirmation of Werner's theories by his work of the last two years, the whole co-ordination theory is quite severely handled by Stewart in his "Recent Advances in Physical and Inorganic Chemistry" (1912, p. 160).

In this connection attention may be called to the work of Costachescu (*Ann. Scient. Univ. Jassy*, vii., 87, 132), who by action of pyridine on ferrous chloride obtains $(FePy_4)Cl_2$. Evaporated with HCl there is formed $(Fe_2.3PyHCl)Cl_6$, or with HBr, $(Fe_2.3PyHBr)Cl_5Br$. With $(Cr(H_2O)_6)F_3$ pyridine gives $\left(Cr\begin{matrix}Py_3\\F_3\end{matrix}\right)$, and by elimination of one pyridine, the aquofluoride, $\left(CrF_3\begin{matrix}Py_2\\H_2O\end{matrix}\right)$. The conductivity of both these compounds is zero, as would theoretically be expected, and neither chromium nor fluorine is precipitable. By the further action of pyridine there were formed salts of the univalent radical $\left(Cr\begin{matrix}Py_4\\Fe_2\end{matrix}\right)$, which acted like a univalent metal.

A study of the equilibrium between purpureo- and roseo-cobalt chlorides,—

$$\left(Co\begin{matrix}Cl\\(NH_3)_5\end{matrix}\right)Cl_2+H_2O \rightleftharpoons \left(Co\begin{matrix}H_2O\\(NH_3)_5\end{matrix}\right)Cl_3,$$

by Lamb and Marden (*Journ. Am. Chem. Soc.*, xxxiii., 1873) shows that this is a monomolecular reaction, and apparently consists in the slow ionisation of the chlorine atom of the purpureo-complex, a water molecule taking its place. By analogy the same thing would be expected in the dissociation of an ordinary electrolyte. In the dry state the roseo-salts have a critical vapour pressure above which only a very slow loss of water occurs, but the change does not appear to be reversible.

A method of investigating residual valence for ammonia in ammoniates is given by Peters (*Zeit. Anorg. Chem.*, lxxvii., 137), which consists in subjecting the dry salt to the action of a measured amount of ammonia in a eudiometer, driving off the ammonia by a vacuum, and then re-saturating it. The results with nearly a hundred salts are tabulated, and the compounds are, in general, what would be expected from Werner's theory, the number of ammonia molecules taken up being most frequently six or a multiple of six. In some cases the ammonia was evidently taken up by both cation and anion, but the distribution could not generally be determined. By this work an interesting line of study has been opened up. Inghilleri (*Atti Accad. Fisiocrit. Siena*, 1909, p. 6) has prepared by the action of quinoline on uranyl salts, a series of complex salts of the general type, $[(C_9H_7N)_2UrO_2]X_2$, including the nitrate, sulphate, acetate, oxalate, and tartrate, as well as double salts. By using aniline in the place of quinoline (*Ibid.*, 1911, p. 3), the sulphate, acetate, and oxalate of the base, $[(C_6H_5NH)_2UrO_2]$, were obtained, as well as the compound, $C_6H_5N.UrO_2.6H_2O$. In connection with complex salts mention should also be made of the continuation of Weinland's work on the chromi-acetates (*Zeit. Anorg. Chem.*, lxxv., 293), where the complex cation contains three chromium atoms with six or less acetate groups, and OH, H_2O, or NH_3. More than a score of different types are described, though they seem as yet not capable of systematisation. In studying the ammoniates of cuprous-mercuric iodides, Anderlini (*Gazz. Chim. Ital.*, [I.], xlii., 321) has prepared $CuHgI_3.2NH_3$, $CuHg_2I_5.3NH_3$, and $CuHg_2I_5.4NH_3$, all of which are rather unstable, and become red on standing in the air.

Ephraim (*Ber.*, xlv., 1322) has made use of the ammoniates in his studies of "Nebenvalenzen." While it

would be difficult to measure directly the force which holds molecular complexes together, it is possible to measure the energy which must be added to decompose them. The decomposition is dependent on pressure, temperature, and the affinity which holds them together. If the pressure is kept constant the temperature of decomposition is a direct function of the energy of formation. This, Ephraim has determined for a large series of ammoniates of the salts of bivalent metals, and finds that the decomposition temperature increases with the decrease in atomic volume of the central (metallic) atom; indeed, the product of the cube root of the decomposition temperature (absolute) by the atomic volume of the central atom is approximately constant. The vapour pressure of the ammoniates can thus be approximately calculated from the atomic volume. The atomic volume is naturally not the only factor which controls the stability of the ammoniates. Thus no metal whose atomic volume is greater than fourteen can form a hexa-ammoniate at ordinary temperature, and no atom except those of the alkaline earths can hold more than six ammonia groups; the octa-ammoniates of these earths must have a special interpretation. The negative atom or group has also something of a determining influence, and the relation between the difference in influence of different negative groups (as Cl-Br) is constant for different metals. Another class of complex salts which is being studied by Copaux (*Zeit. Anorg. Chem.*, lxxiv., 351) and Rosenheim (*Ibid.*, lxxv., 141; lxxvii., 232) as well as by Miolate, is the hetero-poly acids, containing WO_3 and MoO_3. Copaux draws a distinction between what he considers the normal and the secondary basicity of these acids, a distinction which Rosenheim deems unnecessary, and which would, if logically carried out, demand that we should consider phosphoric acid normally dibasic and secondarily tribasic. The free dodeka acids are represented by $H_7[P(W_2O_7)_6].28H_2O$, $H_8[Si(W_2O_7)_6].28H_2O$, and $H_9[B(W_2O_7)_6].28H_2O$, which are isomorphous; the two former of these are metastable at ordinary temperature, and lose water passing into the 22-hydrate. Isomorphous molybdo-phosphoric and molybdo-silicic acids exist, the former also as a 22-hydrate. The 22-hydrates are also isomorphous with each other. The only hydrate of metatungstic acid which Rosenheim could prepare was the 12-tungsto-aquo acid, $H_{10}[H_2(W_2O_7)_6].22H_2O$, though he considers the 28-hydrate probably capable of existence. This metatungstic acid is also isomorphous with the other 22-hydrates. Prandtl has begun (*Ibid.*, lxxiii., 223) the systematisation of the poly acids containing vanadic acid, which seem to be derived from a hexa-vanadic acid, $H_4V_6O_{17}$, whose salts can be made. The seleno-vanadates are derived from this acid with the addition of $4SeO_2$, or in some cases $4H_2SeO_3$, and also with a larger number of SeO_2 molecules, probably with 5, 6, 8, 10, and 12 SeO_2. The NH_4 and K salts of the last, dodeka-selenite, were obtained, and this seems to be the limiting compound. The tungsto- and molybdo-vanadates seem also to be derivatives of the same hexa-vanadic acid.

Finally, under the head of complex compounds mention must be made of further development of the work of Tschugajew (*Comptes Rendus*, cliv., 33) on the platinum bases containing organic sulphides, and of Fritzmann (*Zeit. Anorg. Chem.*, lxxiii., 239) on analogous selenium compounds. The addition of dithioglycoldiethylether to potassium bromo-platinite gives a grey salt, $[Pt.2(C_2H_5.S.CH_2.CH_2.S.C_2H_5)].PtBr_4$, a salt of the type of Magnus's salt. On warming this goes over into the monomeric form, $Pt(C_2H_5.S.CH_2.CH_2.S.C_2H_5).Br_2$. Since the sulphide is bivalent, only the *cis*-form is possible, and no isomer of the monomeric form was found. With methyl (and other) selenides, three isomers (with chloroplatinite) were found, the *cis*- and the *trans*-forms, $\begin{matrix}(CH_3)_2Se\\(CH_3)_2Se\end{matrix}\!>\!Pt\!<\!\begin{matrix}Cl\\Cl\end{matrix}$ and $\begin{matrix}(CH_3)_2Se\\Cl\end{matrix}\!>\!Pt\!<\!\begin{matrix}Cl\\Se(CH_3)_2\end{matrix}$, and also the dimeric form corresponding to Magnus's salt, $[Pt((CH_3)_2Se)_4].PtCl_4$. With diethyltrimethylene diselenide only two isomers were formed, since here, where there are two selenium atoms in the same group, no *trans*-form is possible. This corresponds to the case with ethylenediamine. Many other papers on complex compounds must be passed over, but it is evident that this is to-day the most active field of investigation in inorganic chemistry. In the past, while many of these compounds were known, chemists had to pass them over with possibly an empiric formula. To-day, armed with all the modern refinements of research the chemist is beginning to bring order out of chaos.

In conclusion, it may be noted that nothing further has been heard regarding canadium, the new metal of the platinum group, supposed to have been found in British Columbia. Nor have the efforts to confirm the results of Flint in splitting tellurium by hydrolysis had any positive outcome.

THE SCIENTIFIC WEEK.

(From Our Own Paris Correspondent).

THE LONGEVITY OF MICROBES.

The numerous experiments of M. Trillat and of his pupils had already shown the influence of the presence of gaseous emanations in the air on the longevity of microbes. It is thus that M. Trillat has recognised that the impurities that are daily diffused in the atmosphere, and which proceed from the decomposition of organic matters of animal or vegetable origin, form an extremely favourable environment for the longevity of certain infinitely small microbes. Newly exhaled breath, the emanations of the earth, the neighbourhood of bodies in a state of decomposition, are all sources of gaseous aliments for microbes. The experiments made by M. Trillat on the air of glaciers and air taken in the neighbourhood of habitations have clearly demonstrated this influence. M. Trillat, in collaboration with M. Fouassier, has continued this study which has been presented to the Academy of Sciences by M. Laveran. The two scholars have just shown that the transport of pathogenous microbes in the air is effected especially by the damp which contains, in an infinitesimal state, traces of gas-aliments. Moreover, it would seem that the air when it fulfils certain conditions of dampness, of chemical composition, of temperature, and of age of microbes, is capable of being fertilised directly by the contact of a microbian source. Up till now it was thought, according to numerous observations of the German scholar Flugge, that for microbes to be transported by the air it was necessary to project them into it by some mechanical action, such as pulverisation or any other means, the effect of which would be to detach them from their support. Contrary to this notion, MM. Trillat and Fouassier have established experiments demonstrating that when the superposition of certain factors takes place, the sowing of the air is performed in the same manner as that of a bouillon of culture, merely by the play and movement of the invisible vesicles which constitute the humidity of the air. In an infinitely feeble volume of about one hundred thousandth of a cubic millimetre, these tiny drops are uninfluenced by the action of the force of gravity. They are always mobile under the influence of the least variation of temperature. All these results are of the greatest interest for bacteriological science. MM. Trillat and Fouassier have shown how the contamination of the air takes place in a closed and tranquil space, without the intervention of the presence of dust or of any mechanical means, as was believed up to the present time.

THE MULTIPLICATION OF OYSTERS.

A naturalist of the Natural History Museum, M. Dantan, has shown that the greater number of breeding oysters can breed and produce from their first year. An oyster of twelve or thirteen months old, measuring about 34 mm.,

produces about one hundred thousand larvæ. Oysters of two years of age contain on an average two hundred and fifty thousand, and one of three years of age seven hundred and twenty-five thousand larvæ. In a paper presented to the Academy of Sciences by M. Edmond Perrier, director of the Museum, M. Danton indicates that in oysters of one year the proportion of individuals that give birth to female oysters is very weak. It is only during the third year that oysters approach the normal state of breeding. On the French oyster-beds, where the growth is in the beginning very slow, the reproduction does not begin from the first year. As that appears to be the case of protandric hermaphrodism, while the oyster is laying the greatest number of eggs it is the male sex that predominates.

The Geological Rôle of Fluorine.

A very important communication has been made to the Academy of Sciences by Prof. Armand Gautier on the presence of fluorine in the igneous reactions of the nucleus of the globe. The work of the eminent chemist explains a geological fact misunderstood up till now—the existence of fluorine in all grounds of which it characterises the direct or indirect igneous origin; in the virgin thermal springs, which are formed in the bosom of the igneous rocks, and in the eruptive or volcanic gases in which it had not before been observed. At the present time, M. Armand Gautier has been able to establish the fact that fluorine forms a part of all old rocks, that it always remains in the state of fluorite, apatite, &c., as well as in the waters that flow out of these veins. From all times fluorine has thus come out of the terrestrial nucleus, and it still continues to be produced. But up till now it had been impossible to realise this research in the eruptive gases for want of a method. M. Armand Gautier has succeeded in finding one and also in estimating it. In the month of August last, at an altitude of 1080 metres, at the mouth of the volcano of Vesuvius, he managed to collect the gas of the fumaroles. In it he noticed some fluorhydric acid. He also collected, not far from Voltera, in the Tuscany beds of boracic acid, gases issuing from the soil at 160°, and likewise containing free fluorhydric acid. The condensed water that accompanies these gases contains 3·72 mgrms. of fluorine. So then, whether we examine the old rocks, granites, or porphyries, the soils that proceed from them, the mineral waters that flow from them, or the eruptive gases, always and everywhere fluorine is present and characterises the igneous origin of these products. Fluorine, concludes Prof. Armand Gautier, for want of the means of following it up, has remained up till now the great misunderstood geological and physiological actor.

The Temperature of Arc Lamps.

M. Lummer has just concluded a series of experiments to see if really carbon boils like water; that is to say, if the temperature of ebullition increases when the pressure augments. According to M. Violle, the temperature of the electric arc, in the crater, is the temperature of the volatilisation of carbon. The temperature of the crater of the positive carbon may be estimated at 4000°, that of the negative being from 600° to 700° lower. If the temperature depends upon the pressure it would be possible by increasing this latter to augment the temperature of the arc far beyond the present temperatures. The quantity of light produced would also be greater. The experiments undertaken by M. Lummer seem to prove that it will be possible to arrive at a greater luminous intensity.

Salt Increases the Fertility of the Soil.

Sea-salt seems to play a rather important *rôle* in the development of plants. M. Armand Gautier explains its fertilising properties by the fact that chloride of sodium favours the solubilisation of potassic felspars. M. André, in whose name the paper on the subject is presented to the Academy, adds that carbonate of calcium and sulphate of ammonium do the same. They favour the dissolution in water of the felspars, and of potassic salts, which constitute the mineral aliment of plants.

Radium and Plants.

Recent experiments made in Bohemia and France have led learned men to think that this precious metal, which in a pure state is worth from 700,000 to 800,000 francs per grm., might renovate methods of cultivation. The radioactive properties mixed with the manure seems to serve as a stimulant and to push on the vegetation, giving it at the same time a greater vigour. A great number of experiments made, as well for market-gardening as for the cultivation of wheat, corn, and beet-root, have shown this marvellous action of radium on plants. Other experiments, consisting in the judicious use of radio-active manures in the cultivation of the vine, have had the effect of protecting the vineyards against cryptogamic diseases. Lastly, quite lately, in a paper presented to the Academy of Sciences by M. Maquenne, Professor at the Natural History Museum, M. Stocklasa, of the University of Prague, announces that, according to his personal researches, the radiation and emanation of radium exercise a favourable action on a certain number of microbian species that are of interest to agriculture, especially those that directly fix the nitrogen of the air and those that transform the complex nitrogenised matters into ammonia. It would then seem that the emanation of radium contributes to the increase of the natural fertility of the soil by augmenting its richness in assimilable nitrogen.

PROCEEDINGS OF SOCIETIES.

SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

Ordinary Meeting, November 5th, 1913.

Mr. Leonard Archbutt, President, in the Chair.

Messrs. Charles William Birch, Ulick Richardson Evans, and Harold Warren Gill were elected members of the Society.

Certificates were read for the first time in favour of Messrs. Alan Milsom Bailey, Lanhill, Chippenham, Wilts; Arthur Leslie Barton, 80, Hotham Road, Putney Common, S.W.; Thomas Sidney Haines, 24, Woodfield Avenue, Ealing; and Arthur George Abraham Miller, 1, Pretoria Terrace, Waltham Cross, Herts.

Certificates were read for the second time in favour of Messrs. John Joseph Eastick and J. F. Millar.

The following papers were read and discussed:—

"*Preparation of Rubber for Analysis.*" By L. Archbutt.

The author exhibited a machine for grinding rubber samples and gave some results showing the effect of grinding upon the analytical figures obtained in the analysis of rubber.

Other matters of interest in connection with rubber analysis were also discussed.

"*Examination of Commercial Gelatins in reference to their Suitability for Paper-making.*" By R. W. Sindall and W. Bacon.

Various analytical details of the chemical constituents together with the determination of viscosity and tenacity were dealt with, and more particularly the relation of such physical factors to the actual sizing operations as carried out in the mill.

"*Properties of some Chlorhydrocarbons and their Uses in Chemical Analysis.*" (Part I.). By L. Gowing-Scopes.

The author gives the latest figures for the physical pro-

perties of the chlorethanes and chlorethylenes compared with those of chloroform and carbon tetrachloride. The solubilities of 245 substances, and the action on common metals and inorganic compounds are also given. Their use for fat extractions and their uses in analyses are included, together with a discussion of their chemical properties.

"*Detection and Estimation of Benzoic Acid in Milk and Cream.*" By E. Hinks.

Milk or cream is heated with an equal volume of hydrochloric acid till proteids are dissolved. The fat and benzoic acid are extracted with ether and petroleum ether; the benzoic taken back into ammoniacal water. This solution is tested qualitatively for benzoate, while the benzoic acid may be recovered quantitatively by acidifying, extracting with ether, evaporating spontaneously, and finally subliming in steam oven. The loss on heating gives the benzoic acid.

NOTICES OF BOOKS.

The Cyanide Process of Gold Extraction. By James Park. Fifth English Edition. London: Charles Griffin and Co., Ltd. 1913.

This book belongs to the series of authorised text-books of the Australian Schools of Mines, and is one of the best books on the subject extant. Both the metallurgical process of cyanide extraction and the necessary laboratory control work are fully described in it, and many papers of importance which have appeared in periodical literature or have been read before meetings of scientific societies are reprinted or summarised. For the fifth edition the text has been very carefully revised, and some recent notable advances, such as the process of vacuum filtration, are discussed.

A Text-book of Assaying. By C. and J. J. Beringer. Revised by J. J. Beringer. Thirteenth Edition. London: Charles Griffin and Co., Ltd. 1913.

This text-book on assaying for the use of students of schools of mines and assayers contains full working directions for all the usual methods of assaying, both gravimetric and volumetric, and an excellent course of practical work could readily be based upon it. In the thirteenth edition the assay of wolfram is treated more fully than before, and the sections on the wet assay of tin ores have also been partly re-written.

New Standard Dictionary. London: Funk and Wagnalls, Salisbury Square, Fleet Street, E.C.

This important work produced by Messrs. Funk and Wagnalls, of which we gave a short preliminary notice a few months ago, has now been published, and the two handsome volumes contain a large amount of valuable information resulting from an unusual expenditure of highly skilled labour.

Among the names of the contributors are seen those of Lord Avebury, Sir James Crichton-Browne, Sir Hiram Maxim, Earl Roberts, and many other notable men.

The publishers deserve great credit for their bold originality in the arrangement of the work. They have succeeded in placing the maximum amount of information in such a position that it can be consulted with a minimum expenditure of trouble. Much thought has been given to the important subject of pronunciation, and the definitions given are the outcome of the decisions of a committee of leading experts. In the matter of quotations, which are both lengthy and numerous, the authors' names are always given.

It is the intention of the publishers to combine the advantages of a dictionary and an encyclopædia, and they have largely succeeded in their aim; the two volumes are not too cumbersome to have close at hand, and they will in many cases render the reference to larger works unnecessary.

Cyanamid: Manufacture, Chemistry, and Uses. By Edward J. Pranke, B.Sc. Easton, Pa.: The Chemical Publishing Company. London: Williams and Norgate. 1913.

The author of this monograph has endeavoured to give his readers an unbiased account of the properties and uses of cyanamide, which he believes will play a very important part in the future development of scientific agriculture. Without doubt enough work has been done on the properties and action of this fertiliser to warrant our regarding it as in most respects raised out of the sphere of controversy, although, on the other hand, there is need of further research on some still-disputed questions of detail, and the monograph will serve a double purpose—to give the intending user of the substance a knowledge of its properties and application, and to suggest fresh lines of investigation to the chemist. The decomposition of cyanamide in the soil, and in particular the work of Ulpiani and Kappen, is critically discussed and well summarised, and the question of its toxicity is also treated in an unprejudiced spirit.

Einführung in die Thermodynamik. ("Introduction to Thermodynamics"). By R. Blondlot. Translated by Carl Schorr and Friedrich Platschek. Dresden and Leipzig: Theodor Steinkopff. 1913.

A book which has been translated at the suggestion of Prof. Ostwald can be sure of a good reception in Germany, and the authorised translation of the second French edition of this work will undoubtedly be widely used. Both as regards the material and its presentation and arrangement it is unexceptionable, and for those who are beginning the study of thermodynamics it can be confidently recommended. It contains a complete exposition of the Principle of Equivalence, and Carnot's Principle, giving details of experimental proofs, and explaining their mathematical expression and their application to some natural phenomena. In the last chapter energy is defined and discussed, and the physical significance of the principle of the conservation of energy is explained.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Atti della Reale Accademia dei Lincei.
Vol. xxii. [ii.], No. 2, 1913.

Action of Halogens on Artemisine.—E. Rimini and T. Jona.—Bromine and iodine react with artemisine in exactly the same way as with santonine, if the reaction takes place in presence of the hydracid. Two molecules of artemisine give rise to products in which two atoms of halogen are present in the active state and one in the hydracid form. These substances, the empirical formulæ of which are $C_{30}H_{37}O_8Br_3$ and $C_{30}H_{37}O_8I_3$ respectively, are very unstable, and regenerate artemisine in presence of cold water. With chlorine artemisine reacts differently, a dichlorate of formula $C_{15}H_{20}O_4Cl_2$ being obtained.

Researches on Hydrazones.—L. Vecchiotti.—R. Ciusa has shown that nitrohydrazones can exist in different chromoisomeric modifications. The red form has the malenoid and the yellow the fumaroid structure, and it is obvious that in some cases, *e.g.*, the phenylhydrazine of *o*-nitrobenzaldehyde, the red form will be the more stable. The formation of a pentatomic ring hinders the passage of the malenoid into the fumaroid form.

Vol. xxii., [ii.], No. 3, 1913.

Formula of Chlorhydrate of Apomorphine.—V. Paolini.—Determinations of the water of crystallisation of various specimens of the chlorhydrate of apomorphine obtained from different sources have given as the percentage of water present 4·2, *i.e.*, that calculated from the

formula $C_{17}H_{17}O_2N.HCl + \frac{2}{3}H_2O$. If the chlorine is estimated volumetrically in the anhydrous residue it is found that the formula of the chlorhydrate is undoubtedly $C_{17}H_{17}O_2N.HCl$, and Dott's formula containing C_{34} is not correct. The depression of the freezing-point of the dibenzoyl ether indicates that the formula of apomorphine is the simple formula $C_{17}H_{17}O_2N$.

New Derivatives of Azoxybenzene.—Bruno Valori. —Zinin's *p*-nitroazoxybenzene gives with nitric acid *p*-dinitroazoxybenzene, while with bromine a 2-nitro-4-bromo derivative is obtained. A dibromo-derivative can be prepared by allowing bromine to act upon this substance in a closed tube in presence of a catalyst, such as iron filings. Concentrated sulphuric acid with dibromoazoxybenzene gives dibromoazobenzene, from which the original dibromoazoxy compound can be regenerated by oxidation with hydrogen peroxide in acetic solution. Tribromoazobenzene can be obtained by the action of bromine on dibromoazobenzene.

MISCELLANEOUS.

Institute of Chemistry.—Mr. W. P. Dreaper, F.I.C., will deliver the Second Lecture on "The Research Chemist in the Works, with special reference to the Textile Industry," on Wednesday, November 26th, at 8 p.m., at the Imperial College of Science and Technology, South Kensington, W.; Prof. Raphael Meldola, D.Sc., F.R.S., President, in the Chair.

Lawes and Gilbert Centenary Fund.—It is proposed to erect at Rothamsted a Commemoration Laboratory to celebrate the centenary of the birth of Sir John Lawes in 1814 and of Sir Henry Gilbert in 1817. A sum of £12,000 is required for the purpose, but it is understood that if one-half of this amount can be raised by subscription, the other half will be forthcoming in the form of a grant. An appeal is therefore being issued for the sum of £6000. Subscriptions should be sent to the Secretary, The Rothamsted Experimental Station, Harpenden, cheques being crossed Robarts, Lubbock, and Co.

New Catalogue.—Messrs. A. Gallenkamp and Co., Ltd., of 19—21, Sun Street, Finsbury Square, E.C., have sent a copy of their new catalogue, containing amongst other pieces of apparatus, many recent forms of calorimeters, CO_2 recorders, Haldane's apparatus for the analysis of air in workshops and mine gases, &c. Much space is also given to the various forms of pyrometers that have recently been introduced, particularly the beautiful instruments devised by Prof. Féry. The firm is to be commended for their enterprise in fully illustrating and describing the many novel devices that have recently been placed at the service of chemical and physical science.

MEETINGS FOR THE WEEK.

Wednesday, 26th.—Royal Society of Arts, 8. "Zoological Gardens," by P. Chalmers Mitchell, D.Sc., F.R.S.

Thursday, 27th.—Royal Society. "Method of Measuring the Pressure produced in the Detonation of High Explosives or by the Impact of Bullets," by B. Hopkinson. "Gravitation Instability and the Nebular Hypothesis," by J. H. Jeans. "Diffraction of Light by Particles Comparable with the Wave-length," by B. A. Keen and A. W. Porter. "The Colour of Zircons, and its Radio-active Origin," by R. J. Strutt. "Influence of the Constituents of the Crystal on the Form of the Spectrum in the X-Ray Spectrometer," by W. H. Bragg. "Analysis of Crystals by the X-Ray Spectrometer," by W. L. Bragg.

— Chadwick Public Lectures, 5. (Hartley University College, Southampton). "Military Hygiene, the History of Physical Efficiency in the Army," by Surgeon-Gen. G. J. H. Evatt, C.B.

Friday, 28th.—Physical, 5. "Expansion of Silica" by H. L. Callendar. "Thermal Expansion of Mercury and Fused Silica," by F. J. Harlow. "Experimental Method for the Production of Vibrations on Strings," by J. A. Fleming. Exhibition of a Double-fibre String Galvanometer, by W. Apthorpe.

THE CHEMICAL NEWS

Vol. CVIII., No. 2818.

ANODIC AND CATHODIC RETARDATION PHENOMENA AND THEIR BEARING UPON THE THEORY OF PASSIVITY.*

By G. GRUBE (Dresden).

There used to be a general tendency to assume that both the formation of metallic ions in the anodic dissolution of a metal and the transition from the ionic into the metallic state in cathodic deposition were processes which took place at a practically infinite velocity. On that view a metallic anode, immersed in a solution of one of its salts, should with anodic polarisation pass into solution as soon as the equilibrium potential was slightly exceeded which the respective electrode possessed in that solution. Some rise in the potential above the equilibrium value, and thus some polarisation, was to be expected only in so far as it would be demanded, according to the formula of Nernst, by an increase in the concentration in the immediate neighbourhood of the anode. In cases where a higher polarisation was noticed, such that potentials were attained which permitted of an evolution of oxygen simultaneous with the dissolution of the metal, or merely of an evolution of oxygen unaccompanied by a formation of metallic ions, the cause of this "passivity" was frequently ascribed, with Faraday, to the formation of a film of oxide on the electrode. It was the great merit of M. Le Blanc to have pointed out that, with certain metals, the passivity finds its explanation in the circumstance that these metals emit their ions of lowest valency into the solution at a greatly restricted velocity (*Zeit. Electrochem.*, 1900, vi., 472; "Lehrbüch der Elektrochemie," 1903, 3rd edition, p. 237).

Since now it is a fact that, in the case of one and the same metal which can be rendered passive, the formation of cations takes place at a much more rapid rate when it is in the active state than when in the passive state, we have to ask ourselves how these great variations in the velocity of reaction can arise. There were two possible explanations: either we suppose the rate of formation of ions in the active state to be characteristic of the metal—in that case the retardation of the velocity of reaction in the passive state had to be attributed to the effect of a negative retarding catalyst; or we assume the passive state of metals (which can be passivated) to be the normal state—in that case the marked acceleration in the formation of the ions in the active state could only be due to the effect of some accelerating catalyst. Both these possibilities have been taken into consideration. W. Muthmann and Fraunberger (*Sitzber. Bayer. Akad. Wissensch.*, 1907, xxxiv., 201), as well as Fredenhagen (*Zeit. Physik. Chem.*, 1903, xliii., 1; *Zeit. Elektrochem.*, 1905, xi., 857; *Zeit. Physik. Chem.*, 1908, lxiii., 1) suggested that a solid solution of oxygen is formed on the surface of the metal (which can be rendered passive) when it is anodically polarised or treated with oxidising agents, and that this fact causes the retardation in the emission of ions. F. Foerster (*Abhandlungen Bunsen-Ges.*, 1909, No. 2), on the other hand, advocated that the passive state was normal for certain metals, and that the accelerated formation of cations from these metals in the active state was due to the hydrogen adsorbed by the metallic surface. Foerster was led to this view by the observation, which he and others had frequently made, that whenever iron become active, hydrogen was liberated at it. It was further known that iron, from which hydrogen had once been evolved, could take up small quantities of hydrogen, and would thereby change its properties in the sense that it became highly reactive chemically. The potential of an iron electrode, cathodically polarised with hydrogen, against normal ferrous sulphate also shows less noble values than would correspond to the equilibrium of pure iron with regard to that solution (*Abhandlungen Bunsen-Ges.*, 1909, No. 2, p. 9). The hypothesis hence appears plausible that it is hydrogen which catalytically accelerates the emission of ions from the iron. It will be understood that, like Le Blanc, Foerster finds the cause of the passive state in a diminution of the rate of cation formation. It is a consequence of the strongly retarded formation of ions from metals which can be passivated, that these metals, when anodically polarised, easily assume potentials which correspond to a weak charge of the electrode with oxygen. This oxygen, which in the first instance is a consequence of the passivity, will in its turn be able to impede still more the in itself retarded process of ion-formation at the anode, and will thus lead to a further rise of the anode potential; this potential will finally attain values such that oxygen liberation sets in at the anode in addition to the formation of metallic ions, and that this oxygen liberation may claim the main share of the polarisating current. A complete cessation of the formation of metallic ions owing to the impeding action of the oxygen charge is, however, rare. There will thus be a possibility that the cations emitted from the anode at small rate will combine with the oxygen taken up by the anode surface to oxidic precipitates which, like the oxygen charge, must be regarded as a secondary consequence of the passive properties of the anode metal, not as their cause.

That the fundamental view of the theory of passivity of Le Blanc as just outlined is correct, that is to say, that both anodic dissolution of a metal and cathodic deposition of a metal may be retarded phenomenona, has within recent years been established by many experimental researches (*cf. e.g.*, M. Le Blanc and M. G. Levi, *Annal. d. Physik*, (Boltzmann Festschrift), 1904, p. 183; F. Foerster, *Abhandl. Bunsen-Ges.*, 1909, No. 2; M. Le Blanc, *Ibid.*, 1909, No. 3; A. Schweitzer, *Zeit. Elektrochem.*, 1909, xv., 602; R. Schildbach, *Ibid.*, 1910, xvi., 967; H. G. Byers, *Journ. Am. Chem. Soc.*, 1908, xxx., 1718; E. P. Schoch, *Trans. Am. Electrochem. Soc.*, 1908, xiv., 99; E. P. Schoch and C. P. Randolph, *Journ. Phys. Chem.*, 1910, xiv., 719, &c.).

It would lead us too far to discuss the results of all these researches. I will content myself with dealing with the second part of Foerster's passivity theory, according to which the small velocity of reaction marking the anodic dissolution and the cathodic deposition of passive metals does not alone suffice to focus the whole domain of activation and passivation, and that we are hence forced to assume a co-operation of positive and negative catalysts on the electrode. The following important question thus suggests itself as concerning the problem of passivity:—In how far is the velocity of reaction, and hence the variation of the potential in anodic and cathodic processes, influenced catalytically by the occurrence of small quantities of foreign substances on the surface of the electrode?

I should like now to place before you some experimental researches which F. Foerster and his pupils have undertaken within the past few years in order to answer that question. In the first instance I propose to dwell upon the retardation observed in the emission and deposition of metallic cations; I shall afterwards touch upon the retardation phenomena which occur in the discharge of anions.

Le Blanc (*Abhandl. Bunsen-Ges.*, 1909, No. 3) on the one hand, and F. Foerster and his pupils on the other (*Ibid.*, 1909, No. 2; A. Schweitzer, *Zeit. Elektrochem.*, 1909, xv., 602; R. Schildbach, *Ibid.*, 1910, xvi., 967), had found that the cathodic deposition of the metals of the iron group takes place at a diminished rate. This process now, as F. Foerster has demonstrated in conjunction with

* Communication from the Laboratory for Physical Chemistry and Electrochemistry of the Technical High School, Dresden. (Translated from the German). Contribution to the General Discussion on "The Passivity of Metals" held before the Faraday Society, Nov. 12, 1913.

W. Treadwell, jun., and W. von Escher, may undergo a further retardation when there are also present small quantities of zinc on the surface of the cathodically deposited iron-metal.

The experiments of W. Treadwell ("Dissertation," Zürich, 1909: *cp.* also F. Foerster, *Zeit. Elektrochem.*, 1911, xvii., 883) were undertaken in order to inquire into is in excess, yield a deposit in which zinc predominates; this is so at all the current densities at which any metallic deposits can be secured. The cathode potential assumes during the electrolysis values which come up very close to those of a pure solution of zinc sulphate at corresponding current densities. Fig. 1 exemplifies the results of a series of experiments conducted at 18° with a solution which was

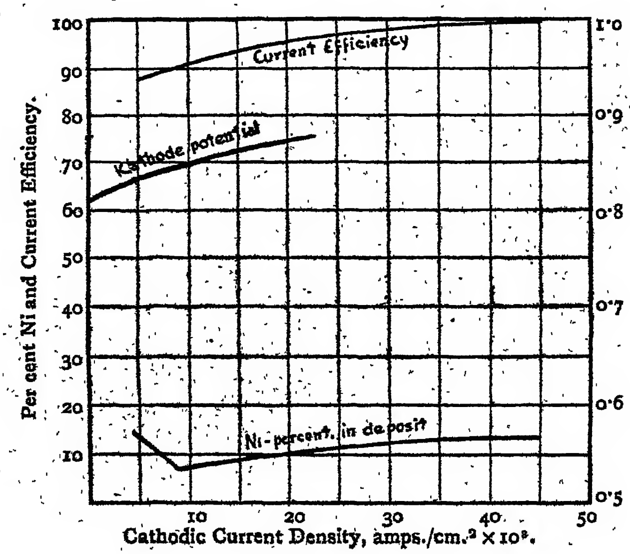


Fig. 1.

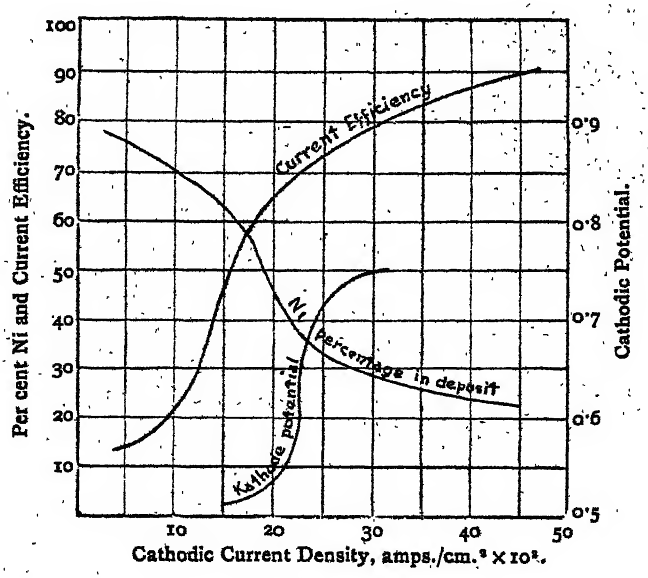


Fig. 2.

the fact which had almost at the same time been established by E. P. Schoch and A. Hirsch (*Journ. Am. Chem. Soc.*, 1907, xxix., 314), that from a solution which contains in addition to an excess of nickel sulphate some zinc sulphate, cathode deposits may be obtained at ordinary temperature which will be decidedly richer in zinc than in nickel. Treadwell's results were the following:—At ordinary temperature solutions, in which the nickel sulphate 0·5 N as regards the zinc sulphate and the nickel sulphate, and 0·01 N as regards the sulphuric acid. The percentage of nickel in the cathode deposit, the cathodic current efficiency, and the variation of the cathode potential with the current density are plotted in the diagram. It will be seen that the nickel percentage is very low even at small current density; the percentage decreases to a minimum, and rises very slowly afterwards. The current efficiency

also rises with increasing current density, from 90 per cent to 95 per cent at high density; thus little current is spent in the generation of hydrogen.

The same solution yields essentially different results at 80°, however, as the experiments plotted in Fig. 2 will show. In this case the deposits, as long as the current density is kept low, are rich in nickel, and resemble nickel in appearance. When the current density is raised, the nickel percentage of the deposit falls off, very rapidly at first, more slowly afterwards. The deposition of the alloy rich in Ni takes place at potentials at which, in the absence of zinc, the solution would have thrown down nickel only. When, however, with increased current density, the Ni percentage of the deposit is lowered and the alloys become richer in Zn, the cathode potential likewise rises suddenly to values approaching that required for the deposition of zinc. The current efficiency curve takes a similar trend. At low current density the efficiency remains below 20 per cent; the current is mainly spent in liberating hydrogen, therefore. When the cathode potential jumps up to that of base metals, with increasing current density, the current efficiency also rises rapidly.

The retardation phenomena occurring in the electrolysis of solutions containing zinc sulphate and ferrous sulphate

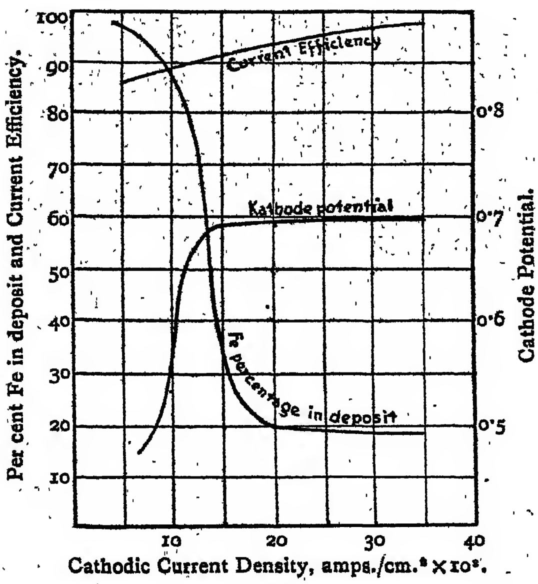


FIG. 3.

are somewhat more pronounced still, as W. von Escher has shown ("Dissertation," Dresden, 1912). If we start from solutions which are equally concentrated as to zinc and iron, the alloys deposited, not only at ordinary temperature, but also at 90°, at very small current density, consist predominantly of zinc. To obtain alloys rich in iron, at low current densities and high temperatures, is only possible when there is a decided excess of ferrous sulphate over the zinc sulphate. Fig. 3 exemplifies an experiment conducted at 90°; the solution was 0·01 N acid, and the ratio of Fe to Zn was 9 : 1·5. Although the temperature was high, it will be recognised the transition from deposits rich in Fe to deposits rich in Zn took place already at very low current density. The deposit potentials were, for the alloys rich in iron, those which (as resulted from special experiments) were required for the deposition of pure iron from solutions of ferrous sulphate of equal concentration. When, however, at higher current densities the transition-point to the deposits consisting essentially of zinc had been passed, the cathode potential assumed the value corresponding to pure zinc. The current efficiency was somewhat below 90 per cent at low current density, and a little above that value at high current density. Further experiments made at the same temperature (90°) showed that when the ratio Fe : Zn was varied in favour of iron, the transition-point from predominantly iron deposits to zinc deposits was shifted into the region of higher current density. In one series of measurements, in which the concentration ratio was Fe : Zn = 9 : 0·63, but which otherwise agreed with the former, the transition occurred only at the density 0·035 or 0·040 amp./cm.². On the other hand, any lowering of the temperature or an increase in the zinc concentration shifted the transition into the region of low current density or suppressed it altogether, the deposits remaining rich in zinc at all the current densities. The concentration of the hydrogen ions also has an influence upon the transition. In a solution of 0·01 N acidity and a concentration ratio Fe : Zn = 9 : 1, the transition was observed at the current density 0·022 amp./cm.² at 90°; in a neutral solution of the same concentration, however, the deposits were poor in zinc up to current densities of 0·040 amp./cm.². In this latter case the transition did not take place therefore. It could be produced, however, also in neutral solutions by raising the zinc concentration. With the concentration ratio Fe : Zn = 9 : 1·5, *e.g.*, the transition was observed at 90°, in neutral solution, between the current densities 0·020 and 0·025 amp./cm.². The zinc proportion of the cathode deposit, at which transition occurred, was 11 per cent, however, whilst 5 per cent sufficed with 0·01 N acidity to raise the potential to the value necessary for the zinc preponderance. The transition was thus more easily realised in the latter case, which is further indicated by the circumstance that a current density of 0·010 amp./cm.² was sufficient.

(To be continued).

ON THE ORIGIN OF SOLAR ELECTRICITY.*

By J. A. HARKER, D.Sc., F.R.S.

MORE than twenty years ago, in his presidential address to the Physics Section of the British Association at Edinburgh, when discussing solar phenomena, Professor Schuster (*Brit. Assoc. Report*, 1892, p. 635) said:—

"May not the periodicity of sun-spots and the connection between two such dissimilar phenomena as spots on the sun and magnetic disturbances on the earth be due to a periodically recurring increase in the electric conductivity of the parts of space surrounding the sun?"

Professor Hale (*Proc. Roy. Inst.*, xix., 621), in his Royal Institution lecture in 1909 on "Solar Vortices and Magnetic Fields," described the methods by which he had detected within the vortices, shown by the spectroheliograph to be present in sun-spots, magnetic fields of considerable strength. In discussing the probable origin of these fields, Hale says:—

"We know from Rowland's experiment that the rapid revolution of an electrically charged body will produce a magnetic field. Thus if a sufficient number of electrically charged particles were set into rapid revolution by the solar vortices, a magnetic field should result. What warrant have we for assuming the existence of charged particles in the sun?"

Some experiments made at the National Physical Laboratory during the past two years by Dr. G. W. C. Kaye (see Note 1) and the writer on the emission of electricity from hot bodies seem to have a distinct bearing on these problems. The application to cosmical phenomena of some deductions from these and a few hitherto unpublished further experiments forms the subject of the present paper.

It may be well briefly to recapitulate here the results

* From *Monthly Notices of the Royal Astronomical Society*, lxxxiii. No. 8.

attained. The first experiments dealt with the electric conductivity of the space inside a carbon-tube resistance furnace heated by alternating current. A pair of small insulated exploring electrodes of carbon projected into the furnace at opposite ends, and were connected with a battery of a few volts and a suitable current-measurer. It was found that, as the furnace was gradually heated from room-temperature, the resistance of the interior space remained practically infinite until a temperature of about 1400° C. was reached, when the resistance commenced to fall rapidly. The curve showing the current between the two exploring electrodes was exponential in character.

It was further found that, on removing the battery, and therefore in complete absence of all applied potential, a transient electric current could be obtained by keeping one of the electrodes in a fixed position in the furnace, and heating or cooling the other by moving it in or out of the hot region. The direction of the current indicated a negative (Note 2) emission from the hotter to the colder surface across the gap (Note 3).

Ionisation currents up to about 3 amperes at over 3 volts were thus obtained from a quite small apparatus, having a working electrode-area of only a few square centimetres. If both electrodes are kept stationary in the furnace, and one is maintained permanently hot, and the other, by means of water-cooling, kept at a much lower temperature, continuous currents of the order of an ampère can be obtained without the application of any potential.

In a later form of the experiment a thin rod of carbon about 15 cm. in length was heated to a very high temperature by low-voltage alternating current; an ionisation current of over 3½ ampères was emitted by the surface of the rod to a comparatively cool insulated carbon tube surrounding it, the current-density in this case exceeding 0·1 ampère per sq. cm. at atmospheric pressure.

The current appears to be associated with the emission from the hot carbon surface of negatively-charged particles. As all the experiments were made at atmospheric pressure, it would seem that these particles must consist almost entirely of sputtered *matter*, and that "corpuscles," whose unencumbered range at such pressures would be extremely small, do not here play the great part in the phenomena they do in high vacua. The evidence to hand in support of this view is discussed in the two memoirs referred to.

In view of the interest of these results obtained with carbon, preliminary experiments on the volatilisation and electric emissivity of a number of metals were made, mostly in nitrogen, at pressures from a few millimetres upwards. The metals were heated by alternating current, and no applied potential was employed. It was found that positive electricity was emitted at temperatures from 1000° to 1400° C. With those metals which melt within this range, a sudden and marked increase in the positive current occurred at the liquefying-point.

At higher temperatures negative electricity predominates, and its quantity increases rapidly with the temperature. With strips of pure iridium, melting between 2300° and 2400° C., which was the metal found to give by far the largest emission, the negative current attained nearly 1-10th of an ampère at the melting-point, the radiating surface being approximately 4 sq. cm. With iron transformer-plate melting at about 1500° C., a large emissivity was often obtained, but with this metal it was found impossible to repeat any given set of conditions sufficiently accurately to obtain even approximately identical results in successive experiments. The negative currents appear to be always associated with considerable sputtering of the metal, and are probably a consequence of some reaction between the metallic surface and the surrounding gas. With carbon the nature, and to some extent also the pressure, of the gaseous atmosphere surrounding the radiating material exerted an influence on the emissivity at the higher temperatures, and with the metals the temperature at which the positive emission changed sign seemed to be greatly influenced by the presence or absence of minute quantities of impurity in the nitrogen atmosphere surrounding the specimen.

From these experiments, and from the known facts regarding the emissions from other materials such as refractory oxides, it would appear that *most substances capable of withstanding a high temperature emit electricity when strongly heated, and that their emissivity when once established increases rapidly with rise of temperature.*

It was obvious from all the experiments that the electric conductivity inside a hot carbon-tube furnace, as evidenced by the ionisation currents produced, was very large, and it is of interest to compare the gaseous conductivity thus manifested with other examples.

A hard Röntgen-ray tube has an apparent resistance of megohms. A quartz mercury-lamp of the usual type has a resistance when running of the order of 50 ohms. In many of these experiments, even with quite small furnaces, the gaseous resistance was measured to be less than 1 ohm at temperatures above 2000° C.; while in one case in a large furnace, where the temperature was pushed to over 3000° C., the apparent resistance fell to microhms, or at any rate to something comparable with that of the graphite rods and of the copper cables forming the rest of the electric circuit. This would mean that *the conductivity of the ionised space was of the same order as if it were filled with mercury or a liquid electrolyte.*

In none of the emission experiments either on carbon or metals up to their melting-point was there any evidence of discontinuity in the law of rapid increase in emissivity with temperature, which was found to hold for the solid substance. Some of the metals, however, showed on melting a marked *increase* in the emission at the moment of fusion.

A word or two may be said here as to the probable velocity and size of the particles which apparently act as carriers in these experiments. In many instances no electric potential was applied, and it seems, therefore, that the particles owe their velocity of emission solely to the temperature. For carbon at 3000° C., according to J. J. Thomson's theory, this velocity should be about 3×10^7 cm. per second, or about a thousandth of that of light, a speed which, compared with that of some corpuscles, is very slow. But, unlike corpuscles, the particles can travel considerable distances in gases even at atmospheric pressure.

If, as we are inclined to believe, it should ultimately prove to be the case that the ionisation currents are carried chiefly by these particles, we have then a means of deducing fairly readily the relation of their charge to their mass (e/m).

An experiment to this end on iridium in nitrogen at 20 mm. pressure, the strip being at a temperature of 1360° C. (black-body), gave the result that the average number of iridium atoms contained in the particle carrying a single negative charge was 1200. In this case, therefore, the mass of the carrier is roughly 5×10^8 times greater than that of a corpuscle, whose mass is 1-1800th of that of a hydrogen atom.

Turning now to the phenomena presented in the sun, it would seem in the light of these facts impossible to avoid the conclusion that *the solar atmosphere is a highly conducting medium.* The most modern determinations of solar temperatures all give values between 5600° and 6000° Abs. (Note 4), estimates much lower than those formerly accepted. From spectroscopic evidence it has been established beyond dispute that iron forms one of the principal constituents of the sun, and carbon a not unimportant one both of the sun and of many stars. For present purposes we will limit our considerations to a discussion of the probable influence on the solar atmosphere of the presence of these two elements.

Iron at its melting-point gave negative currents up to about 15 micro-ampères per sq. cm. in nitrogen at 9 mm. pressure; a rise of temperature of only 60° C. serving to double the current-density over this part of the range.

Even assuming no further increase of emissivity with rise of temperature beyond the melting-point, the current emitted per square kilometre of the area of the photosphere would even on this basis attain 150,000 ampères.

Considering next the case of carbon, if we assume the validity for extrapolation purposes of any such law of increase of conductivity of the space inside a carbon furnace, as that deducible from the data plotted in Fig. 4 of the paper alluded to (Harker and Kaye, *loc. cit.*; *Proc. Roy. Soc.*, 1912, lxxxvi., A, 385), we find that at a temperature far short of that of the sun the conductivity becomes greater than that of any known substance.

Suppose however that, to be on the safe side, we assume in the sun no further increase in emissivity above the figure of 0·1 ampère per sq. cm., actually measured at a temperature approximately 3000° C., this would be more than ample to account for the enormous currents which recent considerations have rendered it probable are circulating in the solar atmosphere.

Hale has shown that it is highly probable that intense magnetic fields of from 2000 to 5000 C.G.S. units are found in sun-spots, and that there is also a general magnetic field of much less intensity existing over the whole body of the sun. Assuming that the circuit producing the field in a spot consists of a single turn, calculation shows that currents of the order of ten million million ampères are required (Note 5).

But at the rate of 0·1 ampère per sq. cm., which is 1000 million ampères per sq. kilo., an area of only 100 × 100 kilometres would alone be required to generate this current, assuming carbon as its source.

As to the mechanism by which the currents *are actually generated* in the solar atmosphere, our present knowledge is very meagre, particularly in view of the great uncertainties as to the physical state of the elements in the sun at the prevailing pressures, also as regards temperature distribution over the surface of the photosphere, and radially outwards through the solar atmosphere. Of the several alternative processes by which the enormous local currents circulating round a sun-spot *might* be generated, that favoured by Hale, the revolution of large numbers of the charged particles by the solar vortices, seems least open to objection.

One obvious direction for further research, before the data here discussed can be properly applied to the elaboration of an electrical solar theory, is the continuation of the experiments on metals beyond their melting- and boiling-points. Indeed, a few preliminary experiments in this direction have already been made. One obstacle at present in the way of their successful completion is to find a material suitable for the construction of the necessary vessels, which is at the same time sufficiently inert and refractory, and which does not itself emit electricity over the temperature range to be studied.

Some indirect evidence on this question of the behaviour of vapours is, however, to hand. It was found that in the experiments with carbon, when a new carbon tube of ordinary commercial quality was heated for the first time, the emission at temperatures in the neighbourhood of 2000° C. was always four or five times as great as in later heatings to the same temperature. It was always observed that, during the first heating in a current of inert gas, the impurities in the carbon, consisting mostly of iron and silicon, are distilled out of the body of the material and carried off in the stream of gas. It was ascertained that this comparatively volatile material all leaves the carbon surface carrying a charge.

In bringing the foregoing facts to the notice of astronomers and cosmical physicists, the writer is fully conscious of many criticisms which may be urged against the conceptions here outlined. But in view of the discoveries of Hale and others, and the consequent interest now being taken in solar phenomena, a presentation of the data even at this early stage in their investigation may not be considered premature.

It may ultimately prove to be the case that such evidence as is here presented, if further supported, may be considered by the authorities as sufficiently conclusive for presuming the existence in the solar atmosphere in very large numbers of electrified particles, by the movements of which enormous currents are generated. Very probably these particles have a mass and velocity widely different from those of corpuscles, the bodies hitherto considered almost exclusively in discussions as to solar currents and magnetism (Note 6). It may therefore, as a consequence, be necessary for cosmical physicists to revise some of their arguments as to the inter-relations of terrestrial and solar magnetic phenomena.

In conclusion, I desire to express my thanks to the Astronomer Royal, to Professor Fowler, and to Dr. W. J. S. Lockyer for their help in references to data and literature.

Notes.

1. Harker and Kaye, "On the Emission of Electricity from Carbon at High Temperatures," *Proc. Roy. Soc.*, 1912, lxxxvi. [A], 379; "On the Electric Emissivity and Disintegration of Hot Metals," *Proc. Roy. Soc.*, June 19, 1913.

2. Positive emissions were obtained with new carbon at low temperatures on first heating, and were probably associated with the expulsion of the first traces of the contained impurities.

3. The hot fixed electrode, being in thermal equilibrium with its surroundings, takes no part in the generation of these currents. The latter may be considered as entirely due to the alternating temperature differences between the surface of the movable electrode and the hotter and colder parts of the furnace-wall immediately surrounding it. It has been conclusively established that the ionisation currents are *not* due to thermo-electricity, or to any rectifying action of the carbon on the alternating currents used for heating the furnace. Many of the effects have been obtained in experiments where the heat-supply has been furnished from non-electrical sources.

4. For example, Abbot, "Measurements on Mount Wilson and Mount Whitney," 5840° Abs. Calculated from an assumed value of Stefan's constant. Also Harker and Blackie, "National Physical Laboratory Report," 1908. 5610° Abs. By total radiation pyrometer directly standardised up to arc temperature, assuming atmospheric absorption 29 per cent.

5. The Astronomer Royal and Mr. Maunder kindly supplied the necessary dimensional data for the spots to enable this computation to be made.

6. See, for example, Schuster, *Proc. Roy. Soc.*, 1911, [1], p. 44; and Birkeland, "The Norwegian Aurora Polaris Expedition," vol. i.; "On the Cause of Magnetic Storms and the Origin of Terrestrial Magnetism," pp. 151 *et seq.*

Colloidal Properties of Hæmoglobin. — Filippo Bottazzi.—The author has prepared pure hæmoglobin by dialysis, when after about five months it is obtained as a red precipitate which refracts light strongly. During dialysis 95 per cent of the hæmoglobin is transformed into meta-hæmoglobin. When perfectly dialysed the latter coagulates at 47—53°. If it is imperfectly dialysed, or in presence of a trace of alkali it becomes opalescent and turbid at that temperature. In presence of an excess of alkali or acid and in absence of neutral salts hæmoglobin is not coagulated by heat. When exposed to the action of an electric field meta-hæmoglobin migrates from cathode to anode, and hence is an electro-negative colloid. The electric conductivity is high. The very low coagulation point suggests that during the transformation of oxyhæmoglobin into meta-hæmoglobin it undergoes a process of polymerisation or condensation.—*Atti della Reale Accademia dei Lincei*, vol. xxii. [ii.], No. 4, 1913.

THE SCIENTIFIC WEEK.

(From Our Own Paris Correspondent).

SOME NEW EXPERIMENTS CONCERNING SPRINGS.

In spite of all the researches that have been made about the mysterious power of spring-finders the problem of source finding remains obscure. Fifteen years ago, in the Laboratory of Marey, Dr. Marage undertook some experiments the object of which was to determine what was true in the phenomenon of the spring finder's wand. These experiments, of a psycho-physiological order, are excessively long, and all those who have studied these questions know the difficulties that are met with before being able to make any serious observations. Having established that this phenomenon seems to be found in a great number of subjects, about one out of ten, Dr. Marage resolved to have recourse preferably to amateurs, absolutely disinterested as to the positive or negative success of the search for springs and having scientific culture. He thus entered into relation with some engineers, and it is the exceedingly interesting results of these experiments that Professor d'Arsonval has presented before the Academy of Sciences. The experiments were tried in Tunis on the side of the roads 38 from Enfidaville to Kairourou and 3 from Enfidaville to Zaghouan. They were made by M. Laudesque, road surveyor, and controlled by civil engineers. As the wand gave him no result, M. Laudesque made use of the pendulum formed, as is well known, by a little sphere or a small conical cylinder suspended at the end of a thread. He was able to determine nine springs of water and to indicate beforehand the depth of the water varying from five to nineteen metres. Soundings were made at the nine points; water was always found, and the depth was recognised as exact at seven points. So there were two errors; the first at the 21st kilometre of the road 38, where water was announced at 13 metres and found at 23 metres, and the second at the 19th kilometre of the road 3, where water was announced at 18 metres and found at 3 metres. The error of depth seems to be due, in the first case, to an incomplete examination of the ground, and in the second case to the width of the subterranean current. In these kinds of researches the negative experiments being often more instructive than the positive, M. Laudesque tried to discover the explanation of the errors he had committed. Dr. Marage thinks that these experiments have the advantage of not giving rise to any criticism on the part of professional spring-finders, who, indeed, contest the value of the results obtained on water channels. Moreover, thanks to the service of roads and bridges, which possesses the means of taking soundings, these researches may be continued in our African colonies. M. Laudesque is quite disposed to give his services to the commission appointed by the Academy of Sciences, composed of Messrs. Armand Gautier, Dastre, Violle, and Douville, in order to make under its direction whatever experiments may be considered useful. In any case the experiments of M. Laudesque are, according to Dr. Marage, the first really well-conducted experiments made on spring-finders, as well as the first having given practical and indisputable results.

THE WORK OF THE INTERNATIONAL BUREAU OF WEIGHTS AND MEASURES.

The fifteenth volume of the memoirs and work of the International Bureau of Weights and Measures has just been presented to the Academy of Sciences by M. Gaston Darboux, perpetual Secretary. We have still fresh in our memory the fine studies of MM. Michelson and Benoit, who have made known to about a millionth degree the fundamental wave-length which the classical work of Rowland had left uncertain to about a 30 thousandth degree. Still further perfecting these methods, MM. Benoit, Fabry, and Perot have been able to simplify, in an enormous proportion, the process of the reduction of the metre to the greatest standard in wave-length. They have also managed to be able to guarantee about the ten-millionth in the values announced to-day, and which by a lucky hazard concord likewise at about the ten millionth with those that were given twenty years ago. M. Ch. Ed. Guillaume gives an account of the determination of standard measures from 1896 to 1904. Lastly the work of the fifth general conference of Paris is resumed at the end of the volume. It was at this conference that the results relative to the mass of the cubic decimetre of water were communicated as well as those concerning the values of the fundamental wave-length. The metrical carat at present accepted everywhere received the first official sanction at this conference.

THE GIACOBINI COMET.

M. Giacobini, astronomer of the Paris Observatory, in a notice presented before the Academy of Sciences by M. Bailland, director of the Observatory, has just made known the elliptical elements of the comet 1913 E. The calculations with the observations made at the observatories of Bamberg, Algiers, and Paris prove without the slightest doubt that this comet is the same as that discovered by Giacobini in 1900. The duration of the revolution of this comet is not more than six years and 464 millionths of a year.

THE EFFECTS OF GUANINE.

Fresh researches on the antagonism of the influences exercised by guanine and andrealine on the constitution have just been made by Professor Desgrez, of the Faculty of Medicine, and by M. Dorléans. In their paper presented by M. d'Arsonval, the two seekers establish that guanine increases the resistance of animals against the toxic action of andrealine, and that it decreases the amount of sugar elimineted under the influence of this substance, so that only traces of it are to be found.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, November 13th, 1913.

Sir ARCHIBALD GEIKIE, K.C.B., President, in the Chair.

PAPERS were read as follows:—

"*The Preparation of Eye-preserving Glass for Spectacles.*" By Sir WILLIAM CROOKES, O.M., F.R.S.

Since March, 1909—in connection with the Glass Workers' Cataract Committee of the Royal Society—I have been experimenting on the effect of adding various metallic oxides to the constituents of glass in order to cut off the invisible rays at the infra-red end of the spectrum, and thus to prepare a glass which will cut off those rays from highly heated molten glass which damage the eyes of workmen, without obscuring too much light or materially affecting the colours of objects seen through the glass when fashioned into spectacles.

Single metals were at first tried in varying quantities to see if from the colour and properties communicated to the glass they were worth further examination. Each specimen is cut and polished into a plate 2 mm. thick. The plate so prepared is first put into the radiometer balance to find the percentage of heat cut off. It is then tested in the spectrum apparatus to ascertain the upper limit of transmission of the ultra-violet rays, next it is tested in Chapman Jones's opacity meter to estimate the percentage of luminous rays transmitted, and finally the colour is registered in a Lovibond's tintometer.

The following elements were selected as likely to be worthy of further experimentation by combining the metals, two, three, or four at a time, in one glass so as to enable the advantages of one to make up for the shortcomings of another:—Cerium, chromium, cobalt, copper,

iron, lead, manganese, neodymium, nickel, praseodymium, and uranium.

Whilst bearing in mind that the chief object of this research is to find a glass that will cut off as much as possible of the heat radiation, I have also attacked the problem from the ultra-violet and the transparency points of view. Taking each of these desiderata by itself I have succeeded in preparing glasses which cut off over 90 per cent of heat radiation, which are opaque to the invisible ultra-violet rays, and are sufficiently free from colour to be capable of use as spectacles. But I have not been able to combine in one specimen of glass these three desiderata in the highest degree. The ideal glass which will transmit all the colours of the spectrum, cutting off the invisible rays at each end, is still to be discovered.

As far as transparency, however, is concerned it will not be an unmixed advantage for the sought-for glass to be quite clear and colourless. The glare of a strong light on white cliffs, expanses of snow, electric light, &c., is known to be injurious to the eye, and therefore a tinted glass combining good obstruction to the heat radiation and ultra-violet rays is the best to aim for.

For ordinary use, when no special protection against heat radiation is needed, the choice will depend on whether the ultra-violet or the luminous are most to be suppressed; or whether the two together are to be toned down. Ordinarily the visible spectrum is assumed to end at the Fraünhofer line K, λ 3933, but light can easily be distinguished some distance beyond by the naked eye. It may therefore be considered that the ultra-violet rays which are to be cut off on account of their possible injurious action are those of shorter wave-lengths than, say, λ 3700. Many glasses have been prepared for this purpose all of which are opaque to rays shorter than λ 3700. The colours are pale green, yellow, and neutral; they transmit ample light so that a choice of tints is available to suit individual taste.

Glasses which are restful to the eyes in the glare of the sun on chalk cliffs, expanses of snow, or reflected from the sea of yellow, green, and neutral tints have also been prepared which have the advantage of cutting off practically all the ultra-violet rays and also a considerable amount of the heat radiation.

"*An Inversion-point for Liquid Carbon-dioxide in regard to the Joule-Thomson Effect.*" By Prof. A. W. PORTER, F.R.S.

"*Negative After-images and Successive Contrasts with Pure Spectral Colours.*" By Prof. A. W. PORTER, F.R.S., and F. W. EDRIDGE-GREEN, M.D.

This paper is a rejoinder to the criticisms made by Prof. Burch to our previous paper. We have repeated our experiments, taking the most minute precautions to avoid all stray light with the same results as before. The most important result is that a negative after-image of an approximately complementary colour is obtained in the total absence of stimuli which would cause such colour.

"*The Positive Ions from Hot Metals.*" By Prof. O. W. RICHARDSON, F.R.S.

"*The Diurnal Variation of Terrestrial Magnetism.*" By G. W. WALKER, F.R.S.

The paper deals with observational data with regard to the diurnal variation of terrestrial magnetism collected from nine observatories.

The data are presented in terms of the Fourier coefficients of the twenty-four hour and twelve hour terms for the geographical components to north, west, and vertical (downwards).

It is noted that the data give strong support to Dr. Schuster's formulæ (*Phil. Trans.*, 1908) for the magnetic potential of diurnal variation as derived from the west component; but the magnetic potential so determined does not give the proper numerical values for the north component as observed.

Two courses are open:—(1) To proceed to higher harmonics; (2) to suppose that the phenomena do not depend entirely of local station time. (1) is discarded partly on account of the trouble of numerical labour, but chiefly because it is likely to lead to unsatisfactory values at the equator or the poles. (2) is tried tentatively and potential functions of simple type are formed which give a general correspondence with the data from these nine stations. More extended data may modify the numerical coefficients.

Without confining oneself to any special theory, the mode of genesis of such potential functions as are suggested by the observations can be specified as related to differential solar action. This is essentially a reversal of Schuster's analytical method. It may stop whenever the data have been accounted for, and thus lead back to the differential conductivity arising from solar action required in Schuster's theory.

The data for vertical force are shown to be in general agreement with Schuster's conclusion that the primary source of variation is of epigene origin.

"*A Suggestion as to the Origin of Black Body Radiation.*" By G. W. WALKER, F.R.S.

The paper first shows that a function of dynamical form can represent the data with regard to radiation quite as well as the formula proposed by Planck.

If the emission at temperature θ in the range of wave-length $\delta\lambda$ is $\phi(\theta, \lambda)\delta\lambda$; then the form—

$$\phi(\theta, \lambda) = k\theta^5 \left(\frac{\lambda\theta}{\lambda^2\theta^2 + a^2}\right)^4$$

satisfies—

1. Stefan's law that the total radiation varies as θ^4.
2. Wien's law that the maximum radiation at any temperature occurs at λ_m, where $\lambda_m\theta$ = constant.
3. The maximum radiation at this wave-length λ_m varies as θ^5.
4. The radiation for great wave-lengths takes Lord Rayleigh's form, varying as $\theta\lambda^{-4}$.
5. It agrees with great closeness with Lummer and Pringsheim's results for short wave-lengths.

It is next shown that the equations of motion for an electron obtained by the author (*Phil. Trans.*, 1910) lead to an emission expression of this quartic type, but in a more general form, which could probably be fitted with the experimental data.

The inference is drawn that the radiation is probably determined by the joint action of a positive and a negative charged particle in stationary orbital motion.

The experimental data are thus brought into accordance with the established principles of dynamical and electro-dynamical theory.

CHEMICAL SOCIETY.

THE Council has ordered the following letter and report to be printed in the *Journal* and *Proceedings* of the Society:—

Whinfield, Salcombe, S. Devon, Sept. 16th, 1913.

GENTLEMEN,—I have the honour to forward the Annual Report of the International Committee on Atomic Weights for 1914, which is submitted for publication in the Society's *Transactions* and *Proceedings*, as hitherto.

The Report deals with all the determinations of atomic weights which have been published since the issue of the preceding Report, but, in accordance with the resolution passed at the Eighth International Congress of Applied Chemistry, it is not proposed to make any change in the official table of atomic weights until the meeting of the next Congress in 1915.

Apart from this, the work of the past year has not shown any necessity for any addition to the existing list of Atomic Weights, or for any substantial alteration in the values last published.

It is accordingly recommended that the table accompanying the Report for 1913 should be reprinted as it stands.

I have appended the signatures of Professors Ostwald and Urbain as desired by them.—I am, Gentlemen, your obedient Servant,

T. E. Thorpe.

The Hon. Secretaries, the Chemical Society, London.

Annual Report of the International Committee on Atomic Weights, 1914.

At the Eighth International Congress of Applied Chemistry, held in New York in September, 1912, a resolution was passed favouring less frequent changes in the official table of atomic weights. Such changes are sometimes embarrassing to technical chemists, and the resolution adopted expressed a desire that the table for 1913 should remain, for legal and commercial use, the official table until the next Congress convenes, in 1915. With this wish the Committee can easily comply; at least, in its essential features, for changes which affect the industrial chemist are not likely to be important, and the text of each annual report will give all the refinements of data which may be needed in theoretical discussions. Only such changes in the table as seem to be absolutely necessary need be made during the next two years, and that they should seriously affect the values in common use is highly improbable.

Since the annual report for 1913 was prepared, a number of important memoirs on atomic weights have appeared, which may be summarised as follows:—

Nitrogen.—Scheuer (*Anzeiger Wien Akad.*, 1912, xlix., 36), from analyses of nitrogen trioxide and tetroxide, and from measurements of ratios connecting the oxides of nitrogen, finds N = 14·008 as the mean of five series of determinations. He also determined the densities of ammonia and of sulphur dioxide, obtaining results in accordance with earlier investigations. The value assigned to N varies from the rounded-off figure given in the table by only 1 part in 7000.

Chlorine.—By the synthesis of NOCl, by the direct union of nitric oxide and chloride, Wourtzel (*Comptes Rendus*, 1912, clv., 345) finds Cl = 35·4596, when N = 14·008. He also (*Comptes Rendus*, 1912, clv., 152) determined the density of nitrosyl chloride, and found the weight of the normal litre to be 2·9919. From this he deduced a molecular weight of 65·456, which is probably too low. From the ratio between ammonia and hydrochloric acid, re-measured by Baume and Perrot (*Comptes Rendus*, 1912, clv., 461), the authors found Cl = 35·463, an unusually high value. None of these new determinations warrants any change in the accepted figure for chlorine.

Bromine.—By the direct synthesis of hydrobromic acid from weighed quantities of hydrogen and bromine, Weber (*Journ. Am. Chem. Soc.*, 1912, xxxiv., 1294) finds Br = 79·3066 when H = 1. With O = 16, the value for bromine becomes 79·924. The accepted value differs from this by only 1 part in 20,000.

Phosphorus.—Baxter and Moore (*Journ. Am. Chem. Soc.*, 1912, xxxiv., 1644), from analyses of phosphorus trichloride, find P = 31·018, in good agreement with previous determinations. This is slightly lower than the value given in the table.

Iron.—By the reduction of ferric oxide in hydrogen, Baxter and Hoover (*Journ. Am. Chem. Soc.*, 1912, xxxiv., 1657) finds Fe = 55·847.

Cadmium.—The electrochemical equivalent of cadmium has been determined by Laird and Hulett (*Trans. Am. Electrochem. Soc.*, xxii., 385), who precipitated cadmium and silver simultaneously in an electric current. From the data given, the atomic weight of cadmium is 112·31, a low value, but one in accord with the previous work of Hulett and Perdue on cadmium sulphate. The investigation is to be continued with the chloride.

Tellurium.—The supposed complexity of tellurium has been re-investigated by Dudley and Bowers (*Journ. Am. Chem. Soc.*, 1913, xxxv., 875), with negative results. They attempted to determine the atomic weight by the basic

International Atomic Weights. (1914).

		O = 16.
Aluminium	Al	27·1
Antimony	Sb	120·2
Argon	A	39·88
Arsenic	As	74·96
Barium	Ba	137·37
Bismuth	Bi	208·0
Boron	B	11·0
Bromine	Br	79·92
Cadmium	Cd	112·40
Cæsium	Cs	132·81
Calcium	Ca	40·07
Carbon	C	12·00
Cerium	Ce	140·25
Chlorine	Cl	35·46
Chromium	Cr	52·0
Cobalt	Co	58·97
Columbium	Cb	93·5
Copper	Cu	63·57
Dysprosium	Dy	162·5
Erbium	Er	167·7
Europium	Eu	152·0
Fluorine	F	19·0
Gadolinium	Gd	157·3
Gallium	Ga	69·9
Germanium	Ge	72·5
Glucinum	Gl	9·1
Gold	Au	197·2
Helium	He	3·99
Holmium	Ho	163·5
Hydrogen	H	1·008
Indium	In	114·8
Iodine	I	126·92
Iridium	Ir	193·1
Iron	Fe	55·84
Krypton	Kr	82·92
Lanthanum	La	139·0
Lead	Pb	207·10
Lithium	Li	6·94
Lutecium	Lu	174·0
Magnesium	Mg	24·32
Manganese	Mn	54·93
Mercury	Hg	200·6
Molybdenum	Mo	96·0
Neodymium	Nd	144·3
Neon	Ne	20·2
Nickel	Ni	58·68
Niton (radium emanation)	Nt	222·4
Nitrogen	N	14·01
Osmium	Os	190·9
Oxygen	O	16·00
Palladium	Pd	106·7
Phosphorus	P	31·04
Platinum	Pt	195·2
Potassium	K	39·10
Praseodymium	Pr	140·6
Radium	Ra	226·4
Rhodium	Rh	102·9
Rubidium	Rb	85·45
Ruthenium	Ru	101·7
Samarium	Sa	150·4
Scandium	Sc	44·1
Selenium	Se	79·2
Silicon	Si	28·3
Silver	Ag	107·88
Sodium	Na	23·00
Strontium	Sr	87·63
Sulphur	S	32·07
Tantalum	Ta	181·5
Tellurium	Te	127·5
Terbium	Tb	159·2
Thallium	Tl	204·0
Thorium	Th	232·4
Thulium	Tm	168·5
Tin	Sn	110·0

		O = 16.
Titanium	Ti	48·1
Tungsten	W	184·0
Uranium	U	238·5
Vanadium	V	51·0
Xenon	Xe	130·2
Ytterbium (Neoytterbium)	Yb	172·0
Yttrium	Yt	89·0
Zinc	Zn	65·37
Zirconium..	Zr	90·6

nitrate method, which they found to be unsatisfactory. A series of syntheses of the tetrabromide gave Te = 127·479.

Uranium.—From calcinations of uranyl nitrate to uranium dioxide, Lebeau (*Comptes Rendus*, 1912, clv., 161) found U = 238·54. Œchsner de Coninck (*Comptes Rendus*, 1912, clv., 1511), by calcination of uranic oxalate, obtained variable results, in mean, U = 238·44.

Scandium.—Atomic weight re-determined by Meyer and Goldenberg (CHEM. NEWS, 1912, cvi., 13), who employed the sulphate method. In mean, Sc = 44·14, in agreement with the accepted value. The higher figure given by Meyer and Winter was due to the presence of thoria in the material employed.

Yttrium.—Two determinations of the atomic weight by Meyer and Wuorinen (*Zeit. Anorg. Chem.*, 1913, lxxx., 7) gave Yt = 88·6. The sulphate method was used. Egan and Balke (*Journ. Am. Chem. Soc.*, 1913, xxxv., 365), in a preliminary study of the ratio between yttrium chloride and yttria, found Yt = 90·12. As their research is to be continued, it would be unwise to use either of these investigations as a basis for changing the table. The lower of the two values appears to be the more probable.

Ruthenium. — Vogt (*Sitzungsber. phys. med. Soc. Erlangen*, xliii., 268), from reductions of ruthenium dioxide, finds Ru = 101·63.

Palladium.—Determinations of atomic weight by analysis of palladiammonium chloride have been made by Shinn (*Journ. Am. Chem. Soc.*, 1912, xxxiv., 1448). The mean value obtained was Pd = 106·709, but the individual determination varied more than is satisfactory. Shinn supposes that the chloride is less definite than it has been assumed to be.

Radium.—From analysis of radium bromide, Hönigschmid (*Monatsh.*, 1913, xxxiv., 283) finds Ra = 225·97, in confirmation of his former analysis of the chloride. The discordance between this value and the higher value obtained by others is unexplained. The presumption is in favour of Hönigschmid's determination, but a change in the table may well be deferred until more evidence is available.

The accompanying table is that of 1913, unchanged.

(Signed) F. W. CLARKE.
W. OSTWALD.
T. E. THORPE.
G. URBAIN.

The following are abstracts of papers received during the vacation, and published, or passed for publication, in the *Transactions* :—

212. "*Viscosity of Cellulose Nitrate Solutions.*" By FRANK BAKER. (*Trans.*, 1913, 1653).

The viscosities of solutions in various solvents of different concentrations of cellulose nitrates have been determined. The relation $\gamma = \gamma_0(1 + ac)k$ was found to express the connection between the concentration of cellulose nitrate (c) and the viscosity. Comparison between the results obtained with different solvents suggests that the values of the constants a and k depend on the solvent power of the liquid for nitrocellulose.

The viscosity of solutions of nitrates of mercerised cellulose suggests that cellulose and mercerised cellulose are not identical, but that cellulose is degraded in the process of solution in ammoniacal copper oxide.

The influence of molecular attraction on physical properties is discussed, and association in liquids ascribed to increased molecular attraction.

213. "*Geranyl Chloride.*" By MARTIN ONSLOW FORSTER and DAVID CARDWELL. (*Trans.*, 1913, 1338).

Geranyl chloride has been prepared by the action of thionyl chloride on a mixture of geraniol and pyridine, and appears to be identical with linalyl chloride; reasons are given for regarding the $C_{10}H_{17}$-nucleus as being that of geraniol rather than the tertiary linanyl group. The *nitrosate*, $C_{10}H_{17}O_4N_2Cl$, melting at 101°, is a convenient derivative by which to identify geranyl chloride, which has a distinct odour of hops, and boils at 103°/14 mm.

The *hydrocarbon*, $C_{10}H_{16}$, produced along with geranyl chloride, boils at 174—176°/763 mm., and yields a *nitrosate*, melting at 131°, whilst the *hydrocarbon*, $C_{10}H_{18}$, prepared by reducing geranyl chloride, boils at 161°/763 mm., and yields a *nitrosate* melting at 95°. *Geranylamine*, $C_{10}H_{19}N$, boils at 105°/19 mm., and forms definite derivatives with the usual agents.

214. "*A New Method of Preparing m-Chlorobenzoic Acid and the Investigation of its Hydroxylamine Salt.*" By WILHELM GLUUD and RICHARD REMPF. (*Trans.*, 1913, 1530).

m-Chlorobenzoic acid is prepared by heating benzoic acid with *aqua regia* on a water-bath, the chloro-acid being separated from the crystalline mass by means of its calcium salt. The hydroxylamine salts of *m*-chlorobenzoic and benzoic acids were also prepared and examined, especially with reference to their solubility and their behaviour on heating. Both salts are easily converted into the corresponding ammonium salts, which readily dissociate into their components, the *m*-chlorobenzoate apparently more readily than the benzoate.

215. "*Contributions to our Knowledge of Semicarbazones. Part III. Action of Heat on the Semicarbazones of Phenyl Styryl Ketone and the Preparation of the Corresponding Phenylsemicarbazones.*" By ISIDOR MORRIS HEILBRON and FORSYTH JAMES WILSON. (*Trans.*, 1913, 1504).

The authors have investigated the action of heat on the phototropic semicarbazones derived from phenyl styryl ketone (compare *Trans.*, 1912, ci., 1482). Both semicarbazones yielded, as main product, an isomeric compound melting at 189°, apparently cyclic in structure, for which the formula—

$$NH\begin{cases} CHPh\text{———}CH \\ \qquad\qquad\quad \| \\ N(CO\cdot NH_2)\cdot CPh \end{cases}$$

is suggested.

The phenylsemicarbazones have also been investigated, having been prepared both directly by the interaction of phenyl styryl ketone and phenylsemicarbazide, and also by the action of boiling aniline on the original semicarbazones. The course of the latter action has been found to depend on the duration of the heating with aniline, prolonged heating producing from both semicarbazones a compound melting at 169°, and apparently, as deduced from spectrographic evidence, analogously constituted to the substance melting at 189°. On the other hand, five minutes' heating with aniline produces colourless phenylsemicarbazones, each semicarbazone yielding its respective phenyl derivative.

These phenylsemicarbazones are strongly phototropic, becoming intensely yellow in light, whilst their solutions show thermotropic properties. The action of sodium ethoxide on the phenylsemicarbazones produces the same effect as light, yellow stereoisomerides being formed.

Various attempts were made to hydrolyse the phenylsemicarbazones, but these only resulted either in a partial conversion of the one stereoisomeride into the other or in the formation of the cyclic compound melting at 189°.

216. "*Contributions to the Chemistry of the Terpenes. Part XVI. The Oxidation of Bornylene with Hydrogen*

Peroxide." By George Gerald Henderson and William Caw. (*Trans.*, 1913, 1543).

Bornylene, in solution in acetic acid, is slowly oxidised by hydrogen peroxide, with the production of a mixture of free acids and esters. The acids were found to be (1) camphenanic acid, $C_9H_{15}{\cdot}CO_2H$ (m. p. 95°); (2) the isomeric *iso*camphenanic acid (m. p. 74°); and (3) a liquid *acid*, which, from the analysis of its *methyl* ester and *silver* salt, appears to have the formula $HO{\cdot}C_8H_{12}{\cdot}CO_2H$. When distilled under diminished pressure this liquid acid is converted into a crystalline unsaturated *acid* (m. p. 80°), which has not been further examined.

The mixture of esters was separated by steam distillation into a volatile and a non-volatile part: The former yielded on hydrolysis (1) acetic acid and, in much smaller quantity, the three acids already mentioned; and (2) a mixture of two alcohols of the formula $C_{10}H_{17}{\cdot}OH$. The alcohol present in largest quantity proved to be borneol, whilst the other was identified as *epi*borneol.

The non-volatile esters when hydrolysed gave (1) acetic acid with much smaller quantities of the other acids, and (2) a mixture of two isomeric *alcohols* of the formula $C_{10}H_{18}O_2$. These alcohols are crystalline solids, which melt at 247—248° and 235—236° respectively; the quantities hitherto obtained were not sufficient to permit of a satisfactory examination of these compounds.

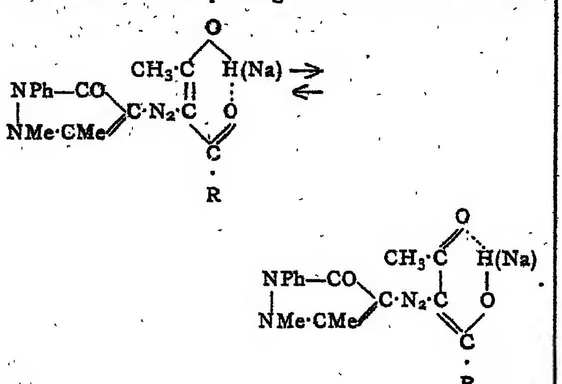
The formation of camphenanic and *iso*camphenanic acids from bornylene is of particular interest, because these acids have already been obtained by oxidising camphene with hydrogen peroxide (compare *Trans.*, 1911, cxcix., 1539). Thus further evidence is afforded of the very close similarity between the molecular structure of bornylene and that of camphene.

217. "*Relative Activities of certain Organic Iodo-compounds with Sodium Phenoxide in Alcoholic Solution.* Part II. iso-, sec.-, *and* tert.-*Alkyl Iodides.*" By David Segaller. (*Trans.*, 1913, 1421).

The reactivities of *iso*butyl, *iso*amyl, *iso*propyl, *sec.*-butyl, *sec.*-amyl, *sec.*-hexyl, *sec.*-heptyl, *sec.*-octyl, *tert.*-butyl, and *tert*-amyl iodides with sodium phenoxide in alcoholic solution have been measured. Allyl iodide was also included to give some indication of the effect of unsaturation. *iso*Compounds are much less reactive than the normal primary isomerides, whereas the normal secondary iodides are only slightly less reactive than the normal primary iodides. The reactivity decreases gradually with increase in molecular weight. The tertiary iodides are the most reactive of the alkyl iodides, and yield olefines when treated with sodium phenoxide.

218. "*Non-aromatic Diazonium Salts.* Part II. *Azo-derivatives from Antipyrinediazonium Salts and their Absorption Spectra.*" By Gilbert T. Morgan and Joseph Reilly. (*Trans.*, 1913, 1494).

The condensation products from antipyrinediazonium salts and acetylacetone, benzoylacetone, and ethyl aceto-acetate and the corresponding sodium derivatives exhibit very similar ultraviolet absorption spectra, their extinction curves being characterised by one persistent band comparable with the band shown by the β-diketones themselves and their metallic derivatives. It is therefore suggested that these condensation products and their sodium compounds are azo-derivatives, having the accompanying co-ordinated configuration.



The corresponding azo-β-naphthylamine and its derivatives were also examined spectroscopically.

219. "*The Ten Stereoisomeric Tetrahydroquinaldinomethylene Camphors.*" By William Jackson Pope and John Reed. (*Trans.*, 1913, 1515).

The *d*- and *l*-tetrahydroquinaldines condense with the *d*- and *l*-oxymethylene camphors, yielding four simple optically active tetrahydroquinaldinomethylene camphors; any two of these latter compounds are capable of combining together to form a stable solid double compound. There are thus obtainable four partly racemic and two fully racemic compounds.

The ten isomeric substances formed have been investigated, and, in spite of the facility with which the partly racemic compounds are produced, externally compensated tetrahydroquinaldine can be resolved by means of its condensation products with *d*-oxymethylenecamphor. The method of resolution is based on the fact that *d*-tetrahydroquinaldine condenses much less rapidly than *l*-tetrahydroquinaldine with *d*-oxymethylenecamphor.

220. "*Isomerism of the Oximes.* Part I. *The Diphenylcarbamyloximes.*" By Oscar Lisle Brady and Frederick Percy Dunn. (*Trans.*, 1913, 1613).

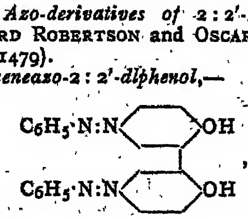
A detailed description of work of which a preliminary account has already appeared (*Proc.*, 1911, xxvii., 239).

221. "*Isomerism of the Oximes.* Part II. *The Nitrobenzaldoximes.*" By Oscar Lisle Brady and Frederick Percy Dunn. (*Trans.*, 1913, 1619).

The authors have investigated the action of sunlight on the nitrobenz*anti*aldoximes, and have shown that in all cases they are converted into the corresponding *syn*-oximes. Hence Ciamician and Silber's statement that the meta-compound does not undergo this change is incorrect. It has also been shown that the *O*-methyl ethers of the nitrobenz*anti*aldoximes are transformed into the *syn*-derivatives by the action of sunlight, but not so readily as are the oximes themselves. Experiments have also been made on the stability of the nitrobenz*syn*aldoximes.

222. "*The Azo-derivatives of* 2:2′-*Diphenol.*" By Philip Wilfred Robertson and Oscar Lisle Brady. (*Trans.*, 1913, 1479).

5:5′-*Bisbenzeneazo*-2:2′-*diphenol*,—



exists in two modifications, yellow and red, both containing half a molecule of water of crystallisation, which is lost only at 160°, the colour of the compounds being unchanged after dehydration.

Several other derivatives have been obtained by the action of 2:2′-diphenol on various diazonium salts, although only the simple benzeneazo-compound has been found to exist in two forms. It has been noticed, however, that these compounds almost invariably separate with water of crystallisation, which is retained with unusual persistency, being driven off but slowly at 160°.

223. "*Constitution of the Trinitro*-p-*aminophenols and Trinitro*-p-*anisidines.*" By Raphael Meldola and Frédéric Reverdin. (*Trans.*, 1913, 1484).

The trinitroacetylaminophenol described in 1906 (*Trans.*, lxxxix., 1935) is the 2:3:6-trinitro- and not the 2:3:5-trinitro-compound, as appeared from the evidence formerly available. The trinitro-*p*-anisidine melting at 127—128°

(*Arch. Sci. phys. nat.*, 1909, [4], xxvii., 383) has now been proved by direct evidence to be the 2 : 3 : 5-trinitro-compound, and the trinitroanisidine melting at 138—139° (*Trans.*, 1910, xcvii., 444) the 2 : 3 : 6-trinitro-compound. The position of the "mobile" nitro-group in the different series has been shown to be as formerly determined, namely, the 3-nitro-group in the 2 : 3 : 6-series, and in the 2 : 3 : 5-series the 2-nitro-group under the influence of bases, sodium acetate, &c., or the 3-nitro-group on diazotisation of the 4-amino group (*Trans.*, 1910, xcvii., 1204).

224. "*New Method for the Determination of the Concentration of Hydroxyl Ions.*" By FRANCIS FRANCIS and FRANK HENRY GEAKE. (*Trans.*, 1913, 1722).

The decomposition of nitrosotriacetonamine into phorone, water, and nitrogen, under the influence of various bases has been fully investigated, the course of the reaction being followed by observing the volume of nitrogen evolved.

The rate of the reaction is proportional to the concentration of the hydroxyl ions, and the results show that, up to a concentration of 0·05N- and beyond 0·3N-hydroxyl ion, a new method has been found for the determination of the concentration of such ions. The utility of this method is indicated by the fact that the effect of neutral salts in moderate concentration on the course of the reaction appears to be negligible.

225. "*Relation between Residual Affinity and Chemical Constitution.* Part IV. *Some Open-chain Compounds.*" By HANS THACHER CLARKE. (*Trans.*, 1913, 1689).

Some measurements have been made of the reactivity of tertiary amines of the general formulæ $Me_2N\cdot[CH_2]_n\cdot NMe_2$ and $MeO\cdot[CH_2]_n\cdot NMe_2$ towards ethyl bromoacetate under standard conditions. It was found that the reactive power of the members of both series increases with increasing length of chain; furthermore, in both cases exaltation of reactivity was observed when the atoms of nitrogen and oxygen were situated in the critical positions ($n = 3$ and 4). These results then tend to confirm the hypothesis of "spacial conjugation" in open-chain compounds. In two control series of the general formulæ $CHMe_2\cdot[CH_2]_n\cdot NMe_2$ and $Et\cdot[CH_2]_n\cdot NMe_2$, only slight variations of reactive capacity were observed in the different members.

226. "*Reduction of Mercuric Chloride by Sodium Formate.*" By ALEXANDER FINDLAY and MORTON JAMES PRYCE DAVIES. (*Trans.*, 1913, 1550).

The reduction of mercuric chloride by sodium formate has been studied kinetically at 40°. From the results it appears that the reaction is a bimolecular one, similarly to the reduction of mercuric chloride by phosphorous acid.

227. "*Volatile Constituents of Coal.*" Part III. By ARTHUR HERBERT CLARK and RICHARD VERNON WHEELER. (*Trans.*, 1913, 1704).

Coal can be separated into two substances, differing widely in their characteristics, by the solvent action, first of pyridine and then of chloroform or benzene. The portion of coal soluble in pyridine appears to consist of the resinous constituents, together with some of the humus substances. The latter are insoluble in chloroform or benzene, whereas the resinous constituents are soluble. A separation can thus be made.

Destructive distillation at different temperatures of the separate portions of a bituminous coal obtained by use of these solvents supports the view already put forward (*Trans.*, 1910, xcvii., 1924; 1911, xcix., 649) that coal is conglomerated of two main types of substances, "hydrogen-yielding" and "paraffin-yielding," the former being the degradation products of the celluloses (humus substances), part of which are insoluble in pyridine, and part soluble in pyridine but insoluble in chloroform; and the latter being the resinous constituents, soluble in both pyridine and chloroform.

In an addendum to the paper [with CLAUDE BERNARD PLATT] attention is drawn to the results obtained by W. J. Russell (*Proc. Roy. Soc.*, 1908, B, lxxx., 432) when investigating the action of resin and allied substances on a photographic plate in the dark, and it is shown that the several portions into which coal can be separated by the solvents pyridine and chloroform affect a sensitised plate in different manners, the results supporting the conclusions drawn from the results of their destructive distillation.

228. "*Volatile Constituents of Coal.* Part IV. *The Relative Inflammabilities of Coal Dust.*" By RICHARD VERNON WHEELER. (*Trans.*, 1913, 1715).

If coal be regarded as a conglomerate of two main types of compounds, the one readily yielding inflammable gases and vapours on heating to a comparatively low temperature, the other requiring a higher temperature of more prolonged duration to decompose it freely, it can be understood that variations in the proportions in which these different types exist in different coals should cause corresponding variations in the chemical and physical properties of the coals.

A property, common to all coals, which would appear to depend essentially on the proportion of readily-decomposed constituents present, is their "inflammability" when in the form of dust.

It is shown that for a number of coal dusts tested the relative inflammabilities varied directly with the relative proportions of readily-decomposed constituents in the coals.

NOTICES OF BOOKS.

Industrial Organic Analysis. By PAUL S. ARUP, B.Sc., A.C.G.I. London: J. and A. Churchill. 1913.

THIS book is intended for the use of the student who has been through a course of theoretical and practical work in pure chemistry and is ready to apply his knowledge to organic technical analysis. It may also be found of use for analytical chemists, serving as a concise work of reference for them, and teachers can learn from it something regarding the nature of the problems with which the practical man has to cope. The intention has been to describe general rather than special methods and complex manufacturing products are not treated, the author limiting himself to the consideration of such materials as coal, petroleum, oils, fats, dairy products, &c. The detection of preservatives in foods is well treated, and the methods chosen for description are well selected. Short theoretical outlines are given as introductions to each chapter, and references to larger treatises are given in great number.

Ensilage. By D. H. DE BURGH. Dublin and London: Maunsel and Company, Ltd. 1913.

THE author of this little book has a first-hand knowledge of the economical aspects of feeding cattle, both for milk and for beef, through the winter months, and the fact that he has come through some hard experiences and had a good many failures gives his advice all the more weight. The book contains explicit directions for building a silo, growing forage plants for it, and making ensilage. The feeding power of ensilage is discussed, and the chapter on this subject will give the farmer and the colonist some food for reflection. If the author writes didactically he appears to have the weight of facts and figures behind his statements, and to have considered the problem of profitable farming, both in Ireland and in Canada, from many different points of view.

Anorganisch-chemisches Praktikum. ("Practical Inorganic Chemistry"). By Dr. G. H. RIESENFELD. Third Edition. Leipzig: S. Hirzel. 1913.

ALTHOUGH this book is intended for beginners it contains a very complete course of analytical work and preparations in inorganic chemistry, and will be found quite detailed enough for first year college students. It is characterised by the very precise directions given for the preparations, while the analytical reactions and separations are fully

explained, with all the formulæ and equations involved. Some general theoretical conceptions are discussed in an introductory chapter, and throughout the book the physico-chemical point of view is emphasised. The tables of separations, both for anions and cations, are novel in some respects, and are very clear and good. A departure from the usual procedure is introduced in treating the most important acids first, their reactions and separations being regarded as easier for the beginner to study than those of the bases.

Eine Anleitung zur Ausführung exakter Physiko-chemischer Messungen bei Höheren Temperaturen. ("An Introduction to Methods of taking exact Physico-chemical Measurements at High Temperatures."). By Dr. F. M. Jaeger. Groningen: J. B. Wolters. 1913.

ALTHOUGH this book is intended primarily to give workers in the author's laboratory an insight into the methods adopted in high temperature research work, and to enable them to be as independent as possible of personal assistance from demonstrators when they first take up their work, it will give any investigator in the same region an excellent review of such work, for it contains very detailed and clear accounts of the most carefully tested and reliable methods of research, especially those which have been worked out by the author and in the geophysical laboratory at Washington. The author believes that faulty methods are to be blamed for the conflicting data which have been accumulated, and he urges the necessity for the employment of trustworthy standard methods only. The determination of high temperatures is first discussed, and then full details are given of the process of determining the temperature of equilibrium, and the optical and thermic data which can be used in the investigation of silicates are tabulated.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clvii., No. 12, September 22; No. 13, September 29; No. 14, October 6, 1913.

These numbers contains no chemical matter.

No. 15, October 13, 1913.

Photo-electric Effect of Metallic Compounds.—B. A. Dima.—The photo-electric effect of analogous compounds of the same metal depends upon the valency of the metal in the compound; the higher the valency the smaller the photo-electric power. It is known that the photo-electric effect diminishes more or less quickly as the duration of exposure is increased. In the case of oxides of the same metal, since the lower oxide has the greater tendency to oxidise, and oxidation corresponds to an increase of valency, the lower oxide ought to exhibit fatigue more strongly to the higher, and this is found to be the case. In the halogen compounds of different metals the effect increases with the atomic weight of the halogen (cadmium is an exception). Potassium chloride and lead iodide and bromide become fatigued as quickly in the light as in the darkness. In the case of potassium bromide the photo-electric effect increases very rapidly in the light and diminishes in darkness, finally returning practically to its initial value. With silver bromide and iodide the same phenomenon is observed, except that the effect is always greater than the initial effect. With silver chloride the effect diminishes after small intervals, both in the light and in the dark.

Leucobases and Dyes of Diphenylethylene.—P. Lemoult.—The gentle oxidation of tetramethyldiamidodiphenylcyclohexylidene methane gives a dye the base of which has the formula $C_{23}H_{30}N_2O$; it fuses at 145°, and readily loses water to give the compound $C_{23}H_{28}N_2$. It corresponds to a dye, the formula of which may be written $C_6H_5(H_4)-C<^{OH}_{(Dm)_2}$; *i.e.*, it is tetrahydrogenated malachite green. The presence of the four supplementary atoms of hydrogen considerably modifies the absorbent powers of the solutions for white light.

Atti della Reale Accademia dei Lincei. Vol. xxii. [ii.], No. 4, 1913.

Structure of 3-Nitroso-2-phenyl-indol.—Luigi Alessandri.—The author has prepared 3-nitroso-2-phenylindol already described by Angeli, and has confirmed his statement that its melting-point is 42°. When ketoximes are heated they undergo the following decomposition:—$3\ {}^{R}_{R'}{>}C{=}NOH = 3\ {}^{R}_{R'}{>}CO + N_2 + NH_3$. Nitrosophenylindol does not give this reaction, but yields a solid isomer melting at 156°. This is a benzoyl derivative formed by the opening of the pyrrol ring, and is isomeric with Pinnow and Sämann's benzoyl derivative. Beckmann's reaction, characteristic of ketoximes, gives positive results when applied to nitrosophenyl-indol.

Formation of Complexes by Alcoholic Hydroxyls.—G. Calcagni.—Glycollic and lactic acids give with iron salts which have the same formulæ as the corresponding salts of chromium, *e.g.*,—

$$\left[Fe_3\begin{matrix}(CH_2OHCOO)_6\\(OH)_2\end{matrix}\right]CH_2OH.COO.Fe(OH)_3.$$

Benzoic and salicylic acids, on the other hand, in the experimental conditions employed by the author, give only simple compounds of iron and chromium, *e.g.*, $Cr\left(C_6H_4<^{OH}_{COO}\right)_3$.

MEETINGS FOR THE WEEK.

MONDAY, Dec. 1st.—Royal Institution, 5. General Meeting.
— Society of Chemical Industry, 8. "Use of Antiseptics for Soil Sterilisation Purposes," by Dr. E. J. Russell and Mr. Buddin.
— Royal Society of Arts, 8. (Cantor Lecture). "The Measurement of Stresses in Materials and Structures," by Prof. E. G. Coker, D.Sc.
— Chadwick Public Lectures, 8.15. (At the Institution of Civil Engineers, Great George Street, Westminster). "House Drainage Law," by W. Addington Willis, LL.B.

WEDNESDAY, 3rd.—Royal Society of Arts, 8. "Perfumery," by J. C. Umney.
— Society of Public Analysts, 8. "Sulphuretted Hydrogen from Artificial Graphite," by W. H. Woodcock and B. Blount. "Determination of Strychnine in the presence of Quinine," by C. Simmonds. "Rate of Liberation of Hydrocyanic Acid from Linseed," by S. Hoare Collins and H. Blair. "Composition of Palm-kernel Oil," by G. Davidson Elsdon.

THURSDAY, 4th.—Chemical Society, 8.30. "Action of Sulphuric Acid on Copper," by (the late) J. T. Cundall. "Reactions which Occur when Glycerol and Oxalic Acid are Heated together whereby Formic Acid and Allyl Alcohol are Produced," by F. D. Chattaway. "Rotatory Dispersive Power of Organic Compounds—Part V., A Comparison of the Optical and Magnetic Rotatory Dispersions in some Optically-active Liquids," by T. M. Lowry, R. H. Pickard, and J. Kenyon. "Organic Derivatives of Silicon—Part XX, Some Condensation Product of Dibenzylsilicanediol," by R. Robison and F. S. Kipping. "Relation between Chemical Constitution and Depth of Colour of Dyes," by E. R. Watson. "Dyes Derived from Quercetin," by E. R. Watson and K. B. Sen. "Improved Form of Apparatus, based on the Landsberger-Sakurai Process, for the Determination of Molecular Weight," by W. E. S. Turner and C. T. Pollard. "Rotation of Optically Active Derivatives of Succinic Acid in Aqueous Solutions of Inorganic Salts," by G. W. Clough.

Literary Intelligence.—Messrs. Longmans, Green, and Co. have in preparation "Chemistry of the Radio-elements Part II. The Radio-elements and the Periodic Law," by Frederick Soddy, F.R.S. This is an extension of the original monograph and covers recent generalisations connecting the radio-active disintegration series with Mendeleeff's Table.

THE CHEMICAL NEWS.

VOL. CVIII., No. 2819.

ANODIC AND CATHODIC RETARDATION PHENOMENA AND THEIR BEARING UPON THE THEORY OF PASSIVITY.*

By G. GRUBE (Dresden).

(Continued from p. 261).

WHEN we summarise the results of Treadwell and Escher we find that in solutions of nickel sulphate and ferrous sulphate, which further contain zinc sulphate, the electrolysis at ordinary temperature yields deposits consisting predominantly of zinc. When the electrolysis is performed at higher temperatures, it is possible under suitable conditions of low current density to obtain also deposits poor in zinc. These latter deposits are realised at low current efficiency and at potentials which would likewise be recorded in depositing pure iron or pure nickel from the same solution not containing any zinc; the formation of the former deposits takes place at considerably higher current efficiency, at the potential necessary for the deposition of zinc.

The explanation of these phenomena may first be given with regard to higher temperatures: at small current density the metals nickel and iron are deposited on the cathode at the potential required for their deposition from pure solutions; at the same time that amount of zinc must be deposited which corresponds to the concentration of the zinc ions at the cathode and to the cathode potential. This amount is in itself very small; since, however, both iron and nickel can absorb a good deal of zinc with formation of alloys, considerable amounts of zinc will have to be deposited in order to get into equilibrium as regards cathode potential and concentration of zinc ions. In this way an alloy poor in zinc is formed at the potential of the more noble metal, and the further deposition of iron or nickel on this alloy is effectually retarded. Consequently the hydrogen liberation will predominate. When now the current density is raised, the concentration of the hydrogen ions in the weakly acid solution will no longer satisfy the current, and polarisation is set up; thus the zinc potential is attained. The hydrogen liberation then diminishes, and zinc is chiefly deposited in addition to some more iron and nickel.

At ordinary temperature the separation of nickel and iron even from their pure solutions is much more difficult than at higher temperature (compare A. Schweitzer, *loc. cit.*, and F. Foerster, *loc. cit.*). The retardation of their deposition from the solutions mixed with zinc sulphate will hence be so great from the very first, that only alloys rich in zinc will result at the zinc potential. Thus the experiments described offer the interesting phenomenon that the cathodic passivity of iron and nickel is so much strengthened by the original co-precipitation of zinc, that the deposition of these metals almost ceases and that, at a potential which is by 0·2 volt less noble than that required for the deposition of pure iron and nickel, a cathode deposit will be formed which will essentially consist of zinc. The intensity of this polarisation apparently depends also on the concentration of the hydrogen ions in the electrolyte, because Escher has proved that the rapid rise in the potential takes place with greater difficulty in neutral than in weakly acid solutions. The acidity of the electrolyte hence acts in the sense of an increase in the zinc concentration, *i.e.*, it intensifies the polarisation.

* Communication from the Laboratory for Physical Chemistry and Electrochemistry of the Technical High School, Dresden. (Translated from the German). Contribution to the General Discussion on "The Passivity of Metals" held before the Faraday Society, Nov. 12 1913.

This fact induced us to compare the polarising effect of zinc with the phenomena which accompany the deposition of iron, cobalt, and nickel from the acid solutions of their simple salts. According to F. Foerster's experiments on iron (*loc. cit.*), those of Schildbach on cobalt (*loc. cit.*), and of M. Schade on nickel ("Dissertation," Dresden, 1912), the deposition potential is in these reactions strongly influenced by the concentration of the hydrogen ions in the electrolyte, the effect being such that increased acidity leads to a higher polarisation, other conditions being equal.

The question now arises, how can we account for the polarisation phenomena accompanying the deposition of the iron metals which, as we have seen, are intensified by the presence of zinc sulphate or of hydrogen ions. Le Blanc has expressed the opinion that the metals form ionic hydrates, whose existence is also assumed for other reasons, and that the supplementary supply of metallic ions (for the deposition of the metal) from these hydrates takes place at a restricted velocity only. On this view the moderate velocity of the reaction—

$$Me_n(H_2O)^{++} \rightleftharpoons Me_n^{++} + H_2O$$

in the direction left to right would be the cause of the high polarisation in the deposition of the metals, and the increase in the polarisation, observed in the presence of zinc sulphate or acid, would occur because these additions much retard the decomposition of the ionic hydrates. Such an inhibitory action is possible; it appears little plausible, however. It seems preferable to look for the cause of the retardation of the cathodic reaction in some change of the cathode surface. We may suppose that alloys containing zinc or hydrogen are deposited on the cathode, and they possess a higher electrolytic solution pressure than the pure nickel or iron. The formation of the—for the present purely hypothetical—intermediate products would then be the cause of the marked retardation in the deposition of the metals.

The experiments which have been mentioned clearly demonstrate, at any rate, that a retarded cathodic process may undergo a further pronounced retardation when the cathode takes up foreign matter. If that be granted, the assumption which is made in explanation of the anodic passivity, namely, that slowly-proceeding anodic reactions are further and essentially retarded by the formation of oxygen alloys in the surface of the anode, gains a higher degree of probability. In addition to this passivity which is due to an oxygen charge, there will also be a possibility of passivity during the anodic dissolution of metals in cases where the cations emitted by the anode will be able to form a scarcely soluble compound with the anions of the electrolyte. We shall only then be justified in ascribing the passivity to surface films if such films may be expected to form in accordance with the chemical behaviour of the electrolyte near the anode. When the causes of the anodic passivity are discussed, the question will therefore not be quite general, whether any retardation in the emission of the ions may arise from the formation of an oxygen alloy on the surface of the anode, or whether the retardation be caused by the mechanical closure (covering up) of the surface of the electrode by the formation of an oxide skin or of some other scarcely soluble precipitate. According to the conditions of the experiment, the one or the other moment will cause passivity.

I now wish to refer to some experiments of mine (*Zeit. Elektrochem.*, 1912, xviii., 189) which show that, at one and the same electrode metal in the same electrolyte, there may, according to the experimental conditions, be a passivity of the surface films, as well as a passivity due to an oxygen charge, and that, under suitable conditions, the two phenomena may continuously pass into one another. The experiments were undertaken, in the first instance, for the purpose of inquiring into the suitability of various metals as electrodes for the electrolytic preparation of ferripotassium cyanide. I determined current density-potential curves with anodes of the several metals in

neutral and in alkaline solutions containing both ferro- and ferripotassium cyanide. The sheet metals were dipped into the electrolyte; the potential was measured first without current; the electrode was then anodically polarised while the electrolyte was well stirred, and the current density was raised, and the potential was determined in the usual way.

We are on this occasion interested only in the results obtained with the metals platinum, gold, iron, nickel, cobalt, and copper. The polarisation phenomena varied to an extraordinary degree with the experimental conditions. When the electrolyte was a neutral solution with a total content (of ferropotassium cyanide + ferripotassium cyanide) of 0·5 mol., whilst the ratio $K_4FeCy_6 : K_3FeCy_6$ in the solution was 25 : 75 or 75 : 25, the potential found, when the current was not flowing, with platinum and gold electrodes was the oxidation potential of the respective solution, whilst much less noble potentials were observed with iron, cobalt, nickel, and copper; these latter potentials gradually became more noble, however. The latter electrodes at the same time became covered with films of their sparely soluble ferrocyanogen compounds. Thus gold and platinum were completely passive in neutral solutions, whilst iron, nickel, cobalt, and copper behaved at first like soluble electrodes which gradually became covered with surface films and assumed the nobler, passive potential. When the electrodes were now anodically polarised, gold and platinum too showed the

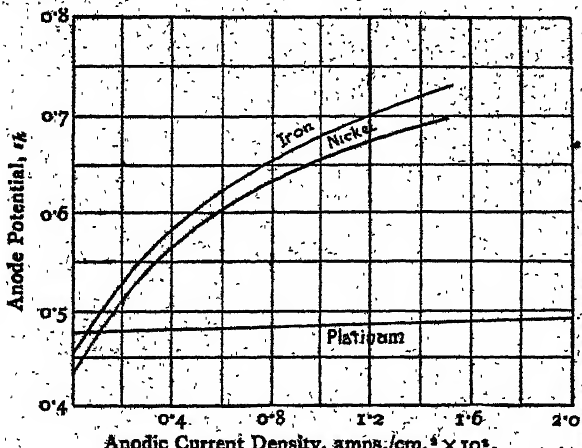


Fig. 4.

small polarisation (due to changes in concentration), whilst an extraordinarily intense polarisation was noticed on the other electrodes, which were covered with surface films. The current density-potential curves observed with iron, nickel, and platinum in neutral solutions are reproduced in Fig. 4. We see how very strong the polarisations are in the first two cases (anodes with surface films) compared with the concentration polarisation of the platinum anode.

The aspect changed very materially when the same solution of ferro- and ferricyanide was rendered 0·1 N alkaline by the addition of KOH. In this solution not only gold and platinum but also iron, cobalt, nickel, and copper marked, when not under current, the oxidation potential of the electrolyte; the appearance of a surface film was no longer noticeable in any case; all the metals remained perfectly bright. When the electrodes were anodically polarised in this instance, the same small concentration polarisation was shown by all the metals except iron. Iron yet indicated in the alkaline solution a pronounced polarisation which could considerably be diminished, it is true, by increasing the alkalinity of the electrolyte and by raising the temperature, but which could never be reduced to the low values measured at the other metals. In these experiments, however, the eye could not discern the formation of any surface film on the iron. But the film was visible when the experiment was made in a 0·01 N alkaline solution. In this solution the iron electrode marked, a short while after immersion, a potential which was by 8 millivolts less noble than the oxidation potential of the solution. Within half an hour, however, the iron potential had risen to this value, while the electrode became covered with a faintly discernible layer of Prussian blue, which was gradually decomposed by the alkali of the electrolyte and converted into an oxide film. This oxide film could only be seen in some spots; the rest of the surface appeared quite bright. Under anodic current this electrode gave a still higher polarisation than had been noticed in the 0·1 N alkaline solution. The existence of an invisible oxide film had, however, to be presumed also in more strongly alkaline solutions, since the polarisation was gradually seen to increase in them when the current intensity was kept constant and the electrolyte remained unchanged. Thus in a 0·1 N alkaline solution, *e.g.*, the polarisation rose, at 0·002 amp./cm.^{2}, in 265 minutes from 90 up to 134 millivolts. These observations indicate that in all probability the passivity of the iron electrode in alkaline ferro-ferricyanide solutions was also due to the formation of an oxide film.

On the contrary, the passivity of electrodes which showed merely concentration-polarisation in alkaline solutions could not be attributed to an oxide film of similar kind as with the iron electrode. This was concluded, in the first instance, from the non-observance of any increasing polarisation, and further from the following experiments:—

When by suitable previous treatment a very thin translucid oxide film had been produced on electrodes of nickel or cobalt, these electrodes showed, in alkaline ferro-ferricyanide solutions, at once the same polarisation phenomena of the same order of magnitude as iron electrodes. If, therefore, the passivity had on nickel, cobalt, and the other metals which were not polarisable in alkaline electrolytes, been caused by the same kind of oxide layers, this passivity should have called forth an intensified polarisation. As this was not the case, we should have been forced—provided we declined to abandon the surface layer as cause of the polarisation—to assume that these surface films responsible for the passivity were good conductors, capable indeed of impeding the emission of cations, but not of opposing any resistance to the passage of the current. The existence of such well-conducting films is, however, extremely improbable, since the oxide skins formed by purely chemical means introduced a considerable polarisation.

If, in spite of that, it should be suggested that the passivity films were of the same kind as those chemically prepared, but of so insignificant a thickness that they could not give rise to any pronounced polarisation, we should have to imagine that the oxidations of ferrocyanide were taking place under the co-operation of some peroxide in the oxide layer. We could not conceive then, however, why such peroxides, whose existence we should have to assume for the different metals gold, platinum, nickel, cobalt, and copper in alkaline solutions, should all be able to effect the oxidation of the ferrocyanide at the same potential and with the same velocity. On account of this equality of the potential, at which the oxidation of the ferro-ferricyanide solutions is taking place with different metals, we shall have to suppose that there is no oxide film on these metals (which cannot anodically be polarised), but that these metallic surfaces are in perfect contact with the electrolyte. Since therefore the presumption of oxide films does not afford any unstrained explanation of the cause of the passivity of platinum, gold, nickel, cobalt, and copper, it appears apposite to trace their passivity back to a retardation in the emission of cations consequent upon the charge of the anode with oxygen.

Such oxygen charges must doubtless exist, to judge

from the position of the potentials of the anodes in the anodic oxidation of ferro-ferripotassium cyanide solutions. We must further suppose these charges to be stronger in alkaline than in neutral solutions, since they must be in equilibrium with the concentration of the hydroxyl ions in the electrolyte. The last-mentioned fact was proved by Fredenhagen (*Zeit. Anorgan. Chem.*, xxix., 396) by comparing the potentials of alkaline ferro-ferripotassium cyanide solutions with the potentials of oxygen electrodes in alkali solutions of equal concentrations. It resulted that the former potentials were more noble than the latter (oxygen) potentials, and that this potential difference increased with increasing alkali concentration of the electrolyte. That shows that the oxygen pressure acting upon an electrode immersed in an alkaline ferro-ferricyanide solution is likewise increased by the higher alkaline concentration of the electrolyte. The pressure is materially smaller in a neutral ferro-ferricyanide solution than in an alkaline solution. Thus it comes about that nickel, cobalt, and copper are still able to emit cations into the electrolyte in neutral ferro-ferricyanide solutions, but that the rate of ion formation has practically dwindled to zero in alkaline solutions, owing to the increased oxygen charge. In the case of iron the rate at which ions can be formed is likewise much diminished in alkaline solutions. It is yet sufficient though to cause the formation of oxide films. The passivity phenomena of the experiments described mainly depend upon the special position of the ferro-ferripotassium cyanide potential, and it is entirely within the range of possibility that, at more noble potentials, the metals examined would show a very different behaviour.

The question in which way the oxygen charge of the anode impedes the emission of cations from the anode cannot yet be answered. If we assume with O. Sackur (*Zeit. Elektrochem.*, 1904, x., 841), as well as with F. Haber and J. Zawadsky (*Zeit. Physik. Chem.*, 1911, lxxviii., 228), that the primary process of the anodic polarisation of a metallic electrode signifies in every case, and therefore also in the case of a soluble anode, the discharge of the anions, then the passivity phenomena which we have been discussing would have to be considered from the same point of view as the retardation of the discharge of halogen ions from platinum electrodes. It has long been recognised (compare E. Müller, *Zeit. Elektro-Chem.*, 1900, vi., 573; 1901, vii., 750; 1902, viii., 424; Luther and Brislee, *Zeit. Phys. Chem.*, 1903, xlv., 216; Böricke, *Zeit. Elektrochem.*, 1905, xi., 71; Pfleiderer, *Zeit. Phys. Chem.*, 1909, xlix.), that, especially with smooth platinum, the discharge of the halogens from solutions of the halides takes place at potentials which are materially more noble than we should expect from the position of the equilibrium potentials of the halogens in the respective solutions.

(To be continued).

The Physical Society's Annual Exhibition.—This Exhibition, which is to be held on Tuesday, the 16th inst., at the Imperial College of Science, South Kensington, will be open in both the afternoon (from 3 to 6 p.m.) and in the evening (from 7 to 10 p.m.). Prof. The Hon. R. J. Strutt, F.R.S., will give a Discourse at 4.30 on "Spiral Electric Discharges"; and Mr. Louis Brennan, C.B., will show some experiments with Soap Films at 8.30 p.m. Some thirty firms will be exhibiting, and there will also be certain experimental demonstrations. We understand that invitations have been given to the Institution of Electrical Engineers, the Institution of Mechanical Engineers, the Faraday Society, the Optical Society, and the Röntgen Society. Admission in all cases will be by ticket only, and therefore Members of the Societies just mentioned (including also the Physical Society) desiring to attend the Exhibition should apply to the Secretary of the Society to which they belong.

THE AMMONIA SYSTEM OF ACIDS, BASES, AND SALTS.*

By EDWARD C. FRANKLIN.

I. *Introduction.*

1. *The Properties of Liquid Ammonia.*—The many striking analogies between liquid ammonia and water as electrolytic solvents have been emphasised by the writer and his co-workers in papers which have appeared from time to time during the past decade. In all those properties which give to water its unique position among solvents, such as its abnormally high boiling-point, its high specific heat, its high heat of volatilisation, its high critical temperature and pressure, its high association constant, its high dielectric constant, and its low boiling-point elevation constant, its power as an electrolytic solvent, and the facility with which it forms compounds with salts, liquid ammonia shows a remarkable similarity to water.

While the boiling-point of liquid ammonia is 33·46° below zero (Gibbs, *Journ. Am. Chem. Soc.*, 1905, xxvii., 851; *cf.*, Franklin, *Ann. Phys.*, 1907, [4], xxiv., 367), it still appears abnormally high when compared with the boiling temperatures of phosphine, arsine, stibine, methane, ethylene, hydrogen sulphide, hydrochloric acid, &c. The specific heat of liquid ammonia (Elleau and Ennis, *Journ. Frank. Inst.*, 1898, cxlv., 189; Dieterici, *Zeit. Kälteind*, 1904) and the heat of fusion (Fourcrand and Massol, *Comptes Rendus*, 1902, cxxxiv., 653, 743) of the solid are greater than the corresponding constants for water or any other known substance, while its heat of volatilisation (Elleau and Ennis, *loc. cit.*; Franklin and Kraus, *Journ. Phys. Chem.*, 1907, xi., 553; Dieterici, *loc. cit.*) with the one exception of water, is the highest of any known liquid. The critical temperature of ammonia is abnormally high, and its critical pressure—the more characteristic constant—is higher than that of any other liquid excepting water. Ammonia is an associated liquid (Franklin and Kraus, *Am. Chem. Journ.*, 1899, xxi., 14; Walden, *Zeit. Phys. Chem.*, 1911, lxx., 599), and its dielectric constant (Goodwin and Thomson, *Phys. Rev.*, 1899, viii., 38; Coolidge, *Wied. Ann.*, 1899, lxix., 125), though much below that of water, is still high when compared with that of non-electrolytic solvents. Its boiling-point elevation constant is the lowest of any known liquid, namely, 3·4 (Franklin and Kraus, *Am. Chem. Journ.*, 1898, xx., 836), as compared with 5·2 for water. In its tendency to unite with salts and other compounds, it probably exceeds water, since salts with ammonia of crystallisation are perhaps even more numerously recorded in the literature than are salts with water of crystallisation. As a solvent for salts it is generally much inferior to water (Franklin and Kraus, *Ibid.*, 1898, xx., 820), though some salts, for example the iodides and bromides of mercury, lead, and silver, dissolve very much more abundantly in ammonia than they do in water, and it far surpasses the latter solvent in its ability to dissolve the compounds of carbon. Finally, it exhibits conspicuous power as an ionising solvent (Note 1), the more dilute ammonia solutions at 33·5° being very much better conductors of electricity than aqueous solutions of the same concentration at 18°.

II. *Metathetic Reactions between Ordinary Acids, Bases, and Salts in Liquid Ammonia Solutions.*

2. *Reactions between Salts.*—The general resemblance between ammonia and water, outlined above, led Franklin and Kraus to inquire whether ordinary metathetic reactions take place in the former solvent as they do in the latter. Such was found to be the case (*Am. Chem. Journ.*, 1899, xxi., 1), with the interesting difference that, as a result of variations in the order of solubilities in ammonia as compared with water, certain reactions take place in the former solvent which do not occur in the latter, or they

* From *American Chemical Journal*, xlvii., No. 4.

may even proceed in opposite directions in the two solvents. As examples may be mentioned the separation of the sulphides of the alkaline earths as white precipitates when liquid ammonia solutions of soluble salts of these metals and ammonium sulphide are brought together, and the precipitation of an alkaline earth chloride when a solution of a soluble salt of any one of these metals is acted upon by a solution of a soluble chloride. The equation $2AgNO_3 + BaCl_2 = Ba(NO_3)_2 + 2AgCl$ read from left to right, represents the familiar action between silver nitrate and barium chloride in aqueous solution. Read from right to left it represents the action of silver chloride on barium nitrate in solution in liquid ammonia. Barium chloride is but slightly soluble in liquid ammonia, while the other three salts are readily soluble.

3. *Reactions between Acids and Bases.*—At first thought it may seem absurd to speak of acids existing in ammonia solutions and reacting therein with bases. Ammonia is frequently referred to as a base, and every one knows that acids unite with ammonia to form the familiar ammonium salts. The fact, however, is to be emphasised that ammonia is not a base, that it is only in the presence of water that ammonia exhibits basic properties, and that in consequence the dry liquid behaves almost, if not quite, as indifferently as water itself towards the ordinary indicators. Now it is an important fact that many ammonium salts of both oxygen acids and halogen acids dissolve freely in the liquid ammonia to form solutions which show certain truly acid properties, as follows:—First, they discharge the red colour of liquid ammonia solutions of phenolphthalein which have been rendered alkaline by the addition of a small quantity of a base; second, solutions of ammonium salts in ammonia attack sodium, potassium, calcium, magnesium, zinc, and cadmium, with the evolution of hydrogen and the formation of the respective metallic salts in accordance with the general equation $M + NH_4Ac = MAc + NH_3 + H$; third, many metallic oxides and certain basic salts—all the members of which two classes of compounds are practically insoluble in ammonia—dissolve in liquid ammonia solutions of ammonium salts. For example, Divers (*Phil. Trans.*, 1873, clxiii., 359) found sodium hydroxide, potassium hydroxide, and the oxides of cobalt, copper, lead, magnesium, mercury, cadmium, and zinc to be soluble in liquid ammonia solutions of ammonium nitrate (Note 2). The writer has confirmed most of these results of Divers, and has also observed the solubility of some of these hydroxides and oxides in solutions of ammonium salts other than the nitrate. It therefore appears that bases dissolve in ammonia solutions of ammonium salts (Note 3) in a manner analogous to the solution of insoluble bases in aqueous acid solutions, as indicated, for example, by the familiar equations—

$$NaOH + NH_4Cl = NaCl + H_2O + NH_3$$
$$Ca(OH)_2 + 2NH_4NO_3 = Ca(NO_3)_2 + 2H_2O + 2NH_3$$

for two of the above mentioned bases.

Even in water solutions the acid properties of ammonium salts are frequently in evidence, as, for example, in the well known cases of the solubility of metallic zinc and magnesium, and of certain metallic oxides, hydroxides, and carbonates, in aqueous solutions of ammonium salts. Especially interesting and significant in this connection, as will be discussed in detail in a subsequent paper, is the conversion of the so-called mercuriammonium compounds into normal mercuric salts by the action of ammonium salts in aqueous solutions.

The reactions which have just been described as taking place in liquid ammonia differ in no essential respects from the familiar metathetic reactions in aqueous solutions. They are reactions between the ordinary oxygen acids, bases, and salts and the halogen acids and salts, taking place in a solvent other than water, a field of study that has received considerable attention from Neumann and his students (*Ber.*, 1910, xliii., 313; Rohland, *Zeit. Anorg. Chem.*, 1898, xviii., 322).

Notes.

1. Cady, *Journ. Phys. Chem.*, 1897, i., 707; Franklin and Kraus, *Am. Chem. Journ.*, 1900, xxiii., 277; Franklin and Cady, *Journ. Am. Chem. Soc.*, 1904, xxvi., 499; Franklin and Kraus, *Ibid.*, 1905, xxvii., 191; Franklin, *Zeit. Phys. Chem.*, 1909, lxix., 272.

It will be observed that it is the hydrides of the first or typical members of the fifth and sixth groups of the Periodic System which show conspicuous power as electrolytic solvents. The hydrides of the other members of these groups (hydrogen sulphide, phosphorus hydride, &c.) show scarcely a trace of such properties. Of the members of the seventh group, Steele, Archibald, and MacIntosh have shown that hydrochloric acid, hydrobromic acid, and hydriodic acid show some considerable power of forming electrolytic solutions. Such relationships, together with the fact that the discovery of fluorine was made possible to Moissan by the observation that potassium fluoride dissolves in liquid hydrofluoric acid to form a conducting solution, suggests that hydrofluoric acid may be as powerful, or possibly even more powerful an ionising agent than water itself. Some of these considerations, together with the facts of its abnormally high boiling-point, its evident association even in the gaseous state, its power of uniting with fluorides as hydrofluoric acid of crystallisation, led the writer, some years ago, to make some preliminary experiments on liquid hydrofluoric acid in the hope that he might see his way to a more extended investigation of liquid hydrofluoric acid as an electrolytic solvent. These preliminary experiments on anhydrous hydrofluoric acid showed it to possess strong solvent powers. Potassium fluoride, sodium fluoride, potassium chloride, sodium bromide, sodium nitrate, sodium chlorate, potassium bromate, acetamide, urea, and potassium sulphate, are abundantly soluble; silver cyanide, barium fluoride, and copper chloride appear to dissolve to some extent; while calcium fluoride, copper sulphate, copper nitrate, ferrous chloride, mercuric oxide, lead fluoride, and metallic magnesium, are insoluble.

2. The so-called Divers liquid, it is to be observed, is simply a concentrated solution of ammonium nitrate in liquid ammonia. The fact that the solution exists at ordinary temperatures at atmospheric pressure is explained as the result of the lowering of the vapour tension of the solvent by the large amount of ammonium nitrate in solution (Kuriloff, *Zeit. Phys. Chem.*, 1898, xxv., 108; Divers, *Ibid.*, 1898, xxvi., 430).

3. The acid properties of ammonium salts in liquid ammonia solutions thus made evident suggest that, analogously, in water solutions of hydrochloric acid the hydrogen ion may be associated with water as OH_3+. Three hydrates of hydrochloric acid of the respective formulæ $HCl.3H_2O$, $HCl.2H_2O$, and $HCl.H_2O$ are known (Rupert, *Journ. Am. Chem. Soc.*, xxxi., 851). Of the latter compound it is interesting to note that Rupert reports it as a "white crystalline substance resembling ammonium chloride in general character."

(To be continued).

Fluorsulphonic Acid and its Salts.—Wilhelm Traube.—Ammonium fluoride reacts energetically with sulphur trioxide, giving a crystalline product, the ammonium salt of fluorsulphonic acid, FSO_3NH_4. The same salt may be obtained by dissolving ammonium fluoride in fuming sulphuric acid, and the free acid may be obtained by distilling the solution. On treating the solution with alcoholic ammonia and evaporating off the alcohol, ammonium fluorsulphonate is formed, and fluorsulphonates are also obtained when dry fluorides are heated with pyrosulphates. They are decomposed by heating with alkalis, but the acid is much more stable towards hydrolysing agents than the analogous chlorsulphonic acid. When salts of fluorsulphonic acid are heated with 99 per cent sulphuric acid in a platinum dish fitted with an upright platinum condenser a good yield of the free acid is obtained.—*Berichte*, xlvi., No. 12.

THE SCIENTIFIC WEEK.

(*From Our Own Paris Correspondent*).

A NEW LAMP FOR ULTRA-VIOLET RAYS.

MM. Billon-Daguerre, Niedard, and Fontaine have just invented a new mercury vapour lamp which acts completely immersed in water and can only work in water. The light, rich in ultra-violet rays, emitted by this lamp does not heat the objects placed near the luminous source. This particular would permit an inflammable film to remain indefinitely in proximity with the lamp without taking fire.

JUPITER'S WHITE SPOT.

The astronomers who study the physical constitution of Jupiter have not yet managed to agree as to the nature of a spot that for a long time went under the name of the "red spot," and which is now white. This mysterious spot has the aspect of an enormous swelling. It occupies an important region of the southern hemisphere of the Jovian planet. The extent of this spot is exceedingly vast. It is about 42,000 kilometres in length. It is very probably formed by gaseous condensations, for the surface of Jupiter is still in a primordial gaseous or liquid state. Contradictory hypotheses have been formed about it. Certain scientists see in this spot of Jupiter a first continent, in formation a thin pellicule that is cooling on the surface of the immense and majestic planet. Other astrophysicists think that this spot is merely constituted by a condensation in the vaporous envelope of Jupiter. An astronomer of the Observatory of Copenhagen, M. Hans Lan, has just published the result of his observations on Jupiter's "red spot." According to this astronomer the visible surface of Jupiter is composed of a vaporous envelope, the gases of which are perhaps very much condensed and form a light yellow layer, with a great power of reflection. Above this is spread a thin layer, which appears to exercise a strong absorption on the under layer. In this very fluid middle formed of clouds and vapours, the spot may be considered, says M. Hans Lan, as a hot lake in the deep layers of the gaseous envelope. The temperature of the spot must be much higher than that of the neighbouring regions. So masses of gas, veritable currents of metals or metalloids fall into it. Its form varies under these influences, but for some years past the red colouring has decreased, the spot has gradually grown pale. It is at present of a brilliant white. The tropical perturbations of the austral hemisphere of Jupiter seem to have an influence on the spot. These perturbations push it from west to east, and M. Quénissel, astronomer at the Flammarion Observatory at Juvisy, has signalled an average advance of about one degree a day. For M. Quénissel the spot is a solidification of the Jovian surface. This is not the opinion of M. Hans Lan. The Danish astronomer states that the disjunction of the spots on Jupiter recalls that of the spots on the sun; their brilliancy varies with the activity of the sun and especially with its magnetic phenomena. These variations of brilliancy have been likewise remarked by M. Fridtjof Le Coultre, an astronomer of Genève. And the gleams that suddenly appear in this reddish region may be attributed either to the lighting up of the Jovian clouds by some volcanic eruption or to some magnetic aurora of extreme intensity. But the problem of the formerly blood-red spot of Jupiter is not yet solved. Is it merely clouds or worlds in a state of formation? Doubtless science will tell us some day what it is.

THE WORLD'S STATISTIC OF TELEPHONE.

An interesting statistic concerning the distribution of telephone throughout the whole world has just been published by the *Lumière Electrique*. The total number of telephonic stations of Europe, Asia, and America was in January, 1912, 12,085,713, whereas on January 1, 1911, there were only 10,919,100 telephones. It was in America that the number of stations increased to such an extent in one year: 760,000 more telephones as compared with an increase of only 200,000 apparatus in Europe. The United States have the greatest number of telephones of any country in the world, with 8,357,625 apparatus, for a population of 92,174,000 inhabitants; that is to say, a telephone post for every 11 inhabitants. Canada follows next with 23 inhabitants per post and a number of 302,759 telephones. Amongst European countries, Denmark holds the first place with 107,153 apparatus for 2,589,000 inhabitants, 1 telephone for every 24 Danes. Sweden and Norway occupy the second and third place. Switzerland comes next with 41 inhabitants per telephonic station. Germany is the fifth with 1,154,518 telephones, or one apparatus for 56 inhabitants. England comes next, followed closely by Luxembourg, Iceland, and Holland. France occupies miserably the tenth place in the European statistic, with 260,998 telephonic posts; that is to say, one apparatus for 150 Frenchmen. The two last ranks are held by Bulgaria, Greece, and Bosnia-Herzegovina, that have only one telephonic apparatus at the disposition of from 1500 to 2000 inhabitants. The ten towns of the whole world that are best provided for as far as is concerned the number of installed telephones are, with the exception of Stockholm, all American. At Los Angeles, at San Francisco, and at Stockholm there is one telephone per 4½ inhabitants, which seems almost incredible, but is in reality rigorously exact.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, November 20th, 1913.

Sir ARCHIBALD GEIKIE, K.C.B., President, in the Chair.

PAPERS were read as follows:—

"*On* Medullosa pusilla." By Dr. D. H. SCOTT, For.Sec.R.S.

"*Neuro-muscular Structures in the Heart.*" By Prof. A. F. S. KENT.

"*Alleged Excretion of Creatine in Carbohydrate Starvation.*" By GEORGE GRAHAM and E. P. POULTON.

1. The presence of aceto-acetic acid always causes an error in the estimation of creatinine, and the error increases with increasing amounts of aceto-acetic acid. As the result of this error the estimation of creatinine will be too low. This error is not eliminated if the diluted urine is allowed to stand for varying lengths of time before making the readings.

2. The aceto-acetic acid is removed in the estimation of creatinine + creatine, and does not cause any error.

3. As the creatinine figure is too low and the creatinine + creatine figure is correct, it will appear that creatine has been excreted.

4. Acetone and oxybutyric acid, if present in amounts comparable to those which usually occur in urine, produce practically no error in the estimation of creatinine.

5. A simple and reliable method has been devised for removing aceto-acetic acid, preliminary to the estimation of creatinine.

6. In our experiments a carbohydrate-free diet did not cause the excretion of any creatine.

"*Origin and Destiny of Cholesterol in the Animal Organism.*" Part XI. *The Cholesterol Content of Growing Chickens under different Diets.* By J. A. GARDNER and P. E. LANDER.

In this paper the authors give an account of determinations of the cholesterol and cholesterol ester content of chickens at various stages of growth and under diets containing different amounts of cholesterol, with a view to ascertaining whether cholesterol can, to any extent, be synthesised in the organism from proteins, fats, or

carbohydrates. The results appear to show that the cholesterol content of the growing chicks depends on the sterol content of the diets, but the figures give no indication that, under the conditions of experiment, cholesterol is synthesised during growth.

The authors consider that the results obtained, taken in conjunction with the fact previously discovered, that in the differentiation of the ovum into the complex aggregates of cells constituting the chick no formation of cholesterol takes place, appear to support the view formerly expressed that cholesterol is not readily synthesised in the organism.

"*Contributions to the Biochemistry of Growth. On the Lipoids of Transplantable Tumours of the Mouse and the Rat.*" By W. E. Bullock and W. Cramer.

Anniversary Dinner, *December 1st, 1913.*

A very large company of eminent men of science was present at the anniversary dinner held in the evening of December 1st at the Hôtel Métropole, at which the new President, Sir William Crookes, O.M., presided. Among those who accepted invitations to be present were:—

The American Ambassador, Sir Archibald Geikie, the Greek Minister, Sir John Simon, Lord Desart, Lord Sumner, Sir Joseph Larmor, M.P., Sir William Ramsay, Sir Aston Webb, Sir Oliver Lodge, Sir E. Ray Lankester, Sir Henry Miers, Sir Francis Younghusband, Sir David Gill, the Hon. Thomas Mackenzie (High Commissioner for New Zealand), the Dean of St. Paul's, the Dean of Westminster, the Vice-Chancellor of Cambridge, Sir Frederic Kenyon, Sir Newton Moore (Agent-General for Western Australia), Sir Thomas Elliott, Sir Frederick Treves, Sir Francis Laking, Sir Ronald Ross, Sir Alfred Kempe, Sir J. Crichton-Browne, Mr. J. H. Balfour Browne, Sir Laurence Gomme, Sir J. Wolfe Barry, Sir Charles Parsons, Sir William Abney, Sir Lauder Brunton, Sir Thomas Barlow, Sir George Robertson, Sir John Murray, Sir Mackenzie Davidson, Sir David Ferrier, Mr. Justice Pickford, Lord Onslow, Sir Alfred Keogh, Sir Thomas Holderness, Sir Alfred Ewing, Sir Reginald Custance, Sir William Tilden, Sir H. Llewellyn Smith, Sir John Bradford, Sir Andrew Noble, Sir John Thornycroft, Sir Edward Troup, Sir Hercules Read, Sir Sydney Olivier, Professor A. Schuster, Sir William Schlich, Sir H. Howarth, the Rev. Dr. Bonney, Dr. A. Smith Woodward, and Professor E. H. Starling.

After the usual loyal Toasts, the American Ambassador, in proposing the toast of "The Royal Society," spoke of the change which had come into the world by reason of the activities that that venerable society had fostered—a change even in our day. Let anyone think, for instance, what it was to live in the pre-Darwinian era as compared with what it was to live in the post-Darwinian era. For his part, he thanked God he was born no earlier than he was. (Laughter). With the rich flowering of science, however, had come a bankruptcy of great literature. He left it to them to say whether these two contemporary phenomena bore the relation of cause and effect. By great literature, of course, he meant not the mere conveying of information, but the great art which used life and thought for its raw materials, and used it with such insight that they called it inspiration, and with such deft artistry that they called it genius. Might not the explanation of this bankruptcy of great literature be that the rise of science, which had changed all our outlook on the world, and had for the first time made us feel at home in this life and unafraid, had for the moment thrown men of great artistic power somewhat out of the use of their powers? It was a pleasing thought to suppose that some member of that society, or some similar body, might make a new era also by the production of great literature, because the great literature of the future must take account of and must be shaped by their view of life under the dispensation of men of science. (Cheers).

The Government and Scientific Problems.

The President said he felt it impossible to express his sense of the distinction they had conferred on him by electing him as their President—the highest reward that could fall to the lot of an English scientific man. The Society's aims are well known to all present, but possibly their needs are not quite so familiar. They are in the not uncommon position of requiring large annual sums to supplement their comparatively small income, which is entirely devoted to the furtherance of scientific knowledge. They have had generous benefactors in the past, and every year the Government places a certain sum of money at their disposal. But they could advantageously dispense, in aid of investigation, very much larger grants than are now in their gift, and they can promise most enthusiastic gratitude to the fortunate possessor of wealth who is yet to come forward with an offer to double or treble their income.

During the past year they had been consulted by the Government on many scientific problems, and they were gratified by the assurance that their advice had been of practical value. They had appointed a sub-committee to prepare the reports of the scientific work of the Terra Nova Antarctic Expedition, and to administer the sum of £17,500 set aside by the Mansion House Committee for that purpose. The Society had also made an investigation into the cause and prevention of glass workers' cataract, and had appointed a committee to administer the small amount of funds granted by the Government for that purpose. They were also proceeding to revise the main features of the magnetic survey of the British Isles, and had appointed a small committee for that purpose.

From his earliest days the Royal Society exerted on him a stimulating influence. It was in 1850—sixty-three years ago—that he first attended a Meeting in the Society's Rooms at Somerset House. More than fifty years ago he was elected a Fellow, and in November, 1863, he was received into the Society by Sir Edward Sabine, and he signed the noted book of Signatures. On the same page as his own occurred the names of Sir William Huggins, Sir Archibald Geikie, Sir Charles [illegible]n, David Livingstone, Sir William Flower, Sir [illegible] Jenner, Lord Tennyson, and Sir John Evans. [illegible] had the extreme honour of being the only chemist—[illegible] the exception of Sir Humphry Davy—who had occupied the Presidential Chair. He had watched the development of chemistry from the stages of observation and classification to the deductive stage of the Newtonian method. He saw now with inward eye, how advances in science research depended upon absolute accuracy of observation, measurement, expression, reasoning, and on scrupulous veracity combined with the widest tolerance of new ideas. And he saw the disdain of scientific teaching—which used to be a characteristic of our industrial leaders—slowly and surely vanishing. This disdain had been replaced by a keen belief in pure research.

After referring to modern progress, he said:—"How extraordinary it is that we have not yet realised that conceivability is not the limit of possibility; that the true opposite of belief in a theory or a fact is not disbelief but doubt, uncertainty, suspension of judgment."

"I wonder," continued Sir William, "what parallel of our appalling ignorance our grandchildren will quote in eighty years' time? What obvious phenomena are overlooked, and what inferences and generalisations are awaiting another Newton? The keen sense of failure, the memory of disappointment and of errors must ever accompany the pursuit of knowledge. Despair is close behind us—enough that it never looks us in the face. But it is unnecessary for me to tell you that it is the work itself that comes first; not the reward. No rejoicings in praise or profit rival the joy of sustained effort, patient labour, even if success does not come at the end to crown the toil. But it is the approbation of the Royal Society that is, indeed, my 'exceeding great reward.'"

Sir JOSEPH LARMOR, in proposing the toast of "The Retiring President," referred to the high literary qualities which Sir Archibald Geikie had combined with profound scientific work, and which had brought the Royal Society into honour and appreciation in circles in which perhaps the hard strenuous routine of difficult scientific work might not have been appreciated on its merits alone.

Sir ARCHIBALD GEIKIE, in responding, said it was not merely an honour to have occupied the chair which was filled by Newton, Sir Humphry Davy, Hooker, Huxley, Kelvin, and Lister. It had been to him a source of the most intense enjoyment and also a great revelation of human nature, chiefly on the pleasant side. It was a great pleasure, indeed, to cultivate friendships with such men as Sir Joseph Larmor himself, Sir Alfred Kempe, Sir Rose Bradford, Prof. Schuster, and all the men with whom he had been associated in the Council. He was deeply indebted to the Royal Society. The only regret which he had to express was that the hope with which he entered upon his Presidency had not been realised, that somehow or other by benefactions—he never looked very much to the State for anything (laughter)—by donations, or bequests, the Royal Society would have been in possession of such a sum, apart altogether from its ordinary income and expenditure, as would enable it to carry out, initiate, and support investigation which at present, for want of funds, it was absolutely unable to do. That had been only partially fulfilled. The Society ought to be in possession of a sum of, say, £1000 a year which it could do what it liked with. He was thinking over these matters when Sir James Caird, of Dundee, sent him a cheque for £5000, expressing the hope that it might possibly be of use in cheapening radium, but fortunately coupled it with this stipulation, "or with any other branch of research which the Society might think it useful to devote it to." Sir J. Caird had been so good as to agree that the fund should be named the "James Caird Fund for Physical Research." That was the sort of fund they wanted—a fund which should not be restricted to any one thing. (Cheers).

The PRESIDENT next proposed "The Medallists," whose names were received with cheers by the company. He prefaced his speech with a few personal remarks, in the course of which he said he hardly dared hope to rival his great predecessor, who, by his personal qualities no less than by his intellectual attainments, had won the esteem and affection of all who had come in contact with him. (Cheers).

Sir RAY LANKESTER, in responding, expressed the thanks of the medallists for the toast which had been honoured. He was very proud to be associated in so doing with the distinguished men to whom medals had that day been awarded. Most of them were his lifelong friends and associates. In the Sylvester Medallist of the year, Dr. Glaisher, he met an old schoolfellow. They were at school together when Colet's School stood near St. Paul's Churchyard. They both owed much to the fact that St. Paul's was an old-fashioned day school where they were little troubled with evening work and had leisure to follow their favourite studies at home. They were all grateful for the generous appreciation of their efforts. The Royal Society had been an *Alma Mater* to him from his boyhood. He had profound reverence for its purpose and method, and pride in its incomparable achievements. (Cheers).

Prof. HAROLD DIXON, who also responded, said the medallists felt that the honour had been paid to them not so much for their own personal achievements, but because they had tried to encourage others to seek out new knowledge. They all rejoiced in that impersonal recognition of their work.

Sir DAVID GILL, in proposing the toast of "The Guests," said they realised that in the American Ambassador they had a man who had helped to promote those international relations in science which were so important for its progress. In coupling the toast with the name of Lord Sumner he said they offered him their warmest congratulations on the recent honour conferred on him. They also congratulated the highest Court of Appeal in the land on a valuable acquisition to its ranks.

LORD SUMNER, in responding, said that never before had he seen assembled in one room so many of the immortals of our race, and never before had he met so many seekers after truth. It was a special pleasure to one of his profession, the members of which did not pursue truth in their sense of the word, to come in contact with so distinguished and ancient a body who devoted themselves to the pursuit of truth for its own sake, and knowledge for its own sake.

CHEMICAL SOCIETY.

(Continued from p. 269).

229. "*Methylation of Cellulose.*" By WILLIAM SMITH DENHAM and HILDA WOODHOUSE. (*Trans.*, 1913, 1735).

When alkali-cellulose, prepared by mixing cellulose with sufficient 15 per cent solution of sodium hydroxide to give a mixture in which the proportions of the constituents are represented by the ratio $C_6H_{10}O_5 : 2NaOH$, is treated with excess of methyl sulphate a methylated cellulose is obtained, which retains the fibrous structure of the original material and has the composition represented by the empirical formula $C_{12}H_{19}O_9{\cdot}OMe$. If this substance is subjected to a repetition of the same treatment the composition of the new product is given by the formula $C_6H_9O_4{\cdot}OMe$, whilst another repetition of the process yields a substance the composition which is given by the formula $C_{24}H_{35}O_{15}(OMe)_5$. All these substances can be acetylated, giving derivatives in which the methyl group is still present. The substance $C_6H_9O_4{\cdot}OMe$ has been converted into a material which resembles viscose.

230. "*Structure of the Salts of Nitrophenols.*" By JOHN THEODORE HEWITT, RHODA MARIANNE JOHNSON, and FRANK GEORGE POPE. (*Trans.*, 1913, 1626).

An attempt has been made to attack the problem of the constitution of the nitrophenolates on chemical grounds. The sodium derivatives of true phenols react in absolute alcoholic solution with ethyl chloroacetate at water-bath temperatures, giving ethyl aryloxyacetates. Even 2:4:6-tribromophenol is not sterically hindered, but *o*- and *p*-nitrophenols do not react under the conditions mentioned. Sodium *m*-nitrophenolate, however, gives a good yield of ethyl *m*-nitrophenoxyacetate.

The nitro-group in the nitrophenolates is evidently also affected; whilst sodium methoxide reduces nitrobenzene to azoxybenzene and nitroanisole to azoxyanisole, the nitrophenols are not converted into azoxyphenols.

231. "*Neutral and Acid Oxalates of Potassium.*" By HAROLD HARTLEY, JULIEN DRUGMAN, CHARLES ARCHIBALD VLIELAND, and ROBERT BOURDILLON. (*Trans.*, 1913, 1747).

A further study has been made of the equilibrium of the system potassium hydroxide-oxalic acid-water, confirming in the main the results of previous investigators, but explaining some discrepancies in their work, for example, the anomalous solubility curve of the neutral oxalate, the degree of hydration of potassium hydrogen oxalate, and the transition temperature of the two modifications of the latter salt. A crystallographic examination has been made of tetrapotassium dihydrogen oxalate, and of a twinned form of the neutral oxalate.

232. "*Adiabatic and Isothermal Compressibilities of some Liquids between One and Two Atmospheres Pressure.*" By DANIEL TYRER. (*Trans.*, 1913, 1675).

A method is described by which the adiabatic compressibility of a liquid can be accurately determined at a pressure of 1 to 2 atmospheres. This consists in principle of compressing the liquid contained in a suitable vessel and observing directly the volume change which occurs, in a calibrated capillary tube. Measurements have been made over a temperature change of 0° to the boiling-poin for the following nine liquids:—Ether, chloroform, carbo

tetrachloride, benzene, toluene, chlorobenzene, carbon disulphide, ethyl alcohol, and water.

By aid of the following thermodynamic equation values have been obtained for the isothermal compressibility:—

$$\beta = \alpha + \frac{T\left(\frac{dv}{dt}\right)^2}{JvC_p},$$

where β is the isothermal compressibility, α the adiabatic compressibility, T the temperature on the absolute scale, v is the specific volume, J the mechanical equivalent of heat, and C_p is the specific heat at constant pressure. The results are compared with the few results already determined by the direct method at low pressures, and a fairly good agreement is found.

233. "*The Constitution of Aconitine.*" By Oscar Lisle Brady. (*Trans.*, 1913, 1821).

A detailed description of work of which a preliminary account has already appeared (*Proc.*, 1912, xxviii., 289).

234. "*Methylation of Quercetin.*" By Arthur George Perkin. (*Trans.*, 1913, 1632).

Although owing to the presence of an hydroxyl group adjacent to the carbonyl group it has not hitherto been considered possible fully to methylate quercetin by means of methyl iodide and alkali, no difficulty in reality exists in preparing a quantity of quercetin pentamethyl ether by this method, provided that an excess of the reagents is employed. This substance is to be found dissolved in the aqueous liquid obtained when the product of the reaction is diluted with water, and may be separated therefrom by treatment with salt. Small amounts of substances soluble in ether are simultaneously produced, namely, *methylquercetin tetramethyl ether*, $C_{20}H_{20}O_7$, yellow needles (m. p. 184—185°), which yields an *acetyl* derivative, $C_{20}H_{19}O_7Ac$, colourless needles (m. p. 178—180°), and a yellow *potassium* salt, decomposed by water, and *methylquercetin pentamethyl ether*, $C_{21}H_{22}O_7$, colourless needles (m. p. 213—215°). By hydrolysis the former gives methylphloroglucinolmonomethyl ether (*Trans.*, 1900, lxxvii., 1318) and veratric acid, whereas from the latter a substance considered to be *methoxymethylfisetol dimethyl ether;* colourless needles (m. p. 148—149°) (compare Herzig, *Ber.*, 1909, xlii., 155), and veratric acid are produced.

235. "*Absorption Spectra of Various Derivatives of Aniline, Phenol, and Benzaldehyde.*" By John Edward Purvis. (*Trans.*, 1913, 1638).

A comparative study has been made of the absorption spectra of the vapours and alcoholic solutions of *o*-, *m*-, and *p*-bromoaniline, *o*-, *m*-, and *p*-iodoaniline, 2 : 4-dichloroaniline, *p*-bromophenol, *p*-iodophenol, 2 : 4 : 6-trichlorophenol, 2 : 4 : 6-tribromophenol, *m*-aminophenol, *m*-dimethylaminophenol, *p*-aminobenzaldehyde, and *p*-dimethylaminobenzaldehyde.

236. "*Chemistry of the Glutaconic Acids.* Part VIII. *β-Phenylglutaconic Acid and the β-Phenyl-α-methylglutaconic Acids.*" By Jocelyn Field Thorpe and Arthur Samuel Wood. (*Trans.*, 1913, 1569).

β-Phenyl-α-methylglutaconic acid has been isolated in three distinct modifications, which can be represented by the following formulæ:—

$$\begin{array}{ccc}
\mathrm{CO_2H{\cdot}CMe} & \mathrm{{\cdot}CMe{:}CO_2H} & \mathrm{CMe{\cdot}CO_2H} \\
\| & | & \| \\
\mathrm{CPh} & \mathrm{CHPh} & \mathrm{CPh} \\
| & | & | \\
\mathrm{CH_2{\cdot}CO_2H} & \mathrm{{\cdot}CH{\cdot}CO_2H} & \mathrm{CH_2{\cdot}CO_2H}
\end{array}$$

(*trans*-Labile acid, m. p. 155°). (Normal acid, m. p. 120°). (*cis*-Labile acid, m. p. 108°).

The *trans*-labile acid is stable towards acetyl chloride, but both the normal acid and the *cis*-labile acid are converted by this reagent into the hydroxy-anhydride (I.) (m. p. 94°), which yields the anilic acid (II.) (m. p. 143°), and the hydroxy-anil (III.) (m. p. 216°) with aniline.

$$\mathrm{CPh}\begin{array}{l}=\mathrm{CMe{-\!\!-\!\!-}CO}\\ \diagdown\,\mathrm{CH{:}C(OH)}\end{array}\!\!>\mathrm{O} \qquad \mathrm{CPh}\begin{array}{l}=\mathrm{CMe{\cdot}CO_2H}\\ \diagdown\,\mathrm{CH_2{\cdot}CO{\cdot}NHPH}\end{array}$$

(I.) (II.)

$$\mathrm{CPh}\begin{array}{l}=\mathrm{CMe{-\!\!-\!\!-}CO}\\ \diagdown\,\mathrm{CH{\cdot}C(OH)}\end{array}\!\!>\mathrm{NPh}$$

(III.)

The *trans*-labile acid is converted into the sodium salt of the *cis*-labile acid by alkali hydroxide, and both the *cis*-labile acid and the *trans*-labile acid are converted into the normal acid by hydrochloric acid. The hydroxy-anhydride is converted into the normal acid by boiling water and into the *cis*-labile acid by alkali in the presence of casein. The three modifications of the acid are readily distinguished by the aid of their barium salts.

The acids of this type readily undergo decomposition when boiled with dilute mineral acids, and yield the corresponding hydrocarbon, thus:—

$$\begin{array}{c}\mathrm{{\cdot}CH{\cdot}CO_2H}\\ |\\ \mathrm{CHPh}\\ |\\ \mathrm{{\cdot}CH{\cdot}CO_2H}\end{array} \longrightarrow 2\mathrm{CO_2} + \begin{array}{c}\mathrm{CH_2}\\ \|\\ \mathrm{CPh}\\ |\\ \mathrm{CH_3}\end{array}$$

(β-Phenylglutaconic acid). (*iso*Propenylbenzene).

237. "*The Chemistry of the Glutaconic Acids.* Part IX. *A Method for Distinguishing between the Esters of the Normal and Labile Acids.*" By Jocelyn Field Thorpe and Arthur Samuel Wood. (*Trans.*, 1913, 1579).

The ester of a labile acid can be readily distinguished from its normal isomeride by the capacity it possesses of forming a condensation product with ethyl sodiocyanoacetate; thus the labile ethyl ester of β-methylglutaconic acid forms the condensation product (I.) to the extent of 60 per cent, whereas the corresponding normal ester under similar conditions yields no trace of this substance:—

$$\begin{array}{lll}
\mathrm{CH{\cdot}CO_2Et} & \mathrm{CH_2{\cdot}CO_2Et} & \mathrm{CH_2{\cdot}CO_2H} \\
\| & | & | \\
\mathrm{CMe} & \mathrm{CMe{\cdot}CH(CN){\cdot}CO_2Et} & \mathrm{CMe{\cdot}CH_2{\cdot}CO_2H} \\
| & | & | \\
\mathrm{CH_2{\cdot}CO_2Et} & \mathrm{CH_2{\cdot}CO_2Et} & \mathrm{CH_2{\cdot}CO_2H}
\end{array}$$

(Labile ester.) (I.) (II.)

The condensation product yields *ββ-dimethylpropanetricarboxylic acid* (II.) on hydrolysis, and derivatives of this compound have been prepared. Several normal esters of the series were investigated, but were found to yield no trace of a condensation product. Normal ethyl glutaconate, which is capable of passing, with considerable ease, into derivatives of the unstable labile ester, yields with ethyl sodiocyanoacetate about 5 per cent of the condensation product (III.) from which *isobutane-αγγ′-tricarboxylic acid* (IV.) can be isolated on hydrolysis:—

$$\begin{array}{ll}
\mathrm{CH{\cdot}CO_2Et} & \mathrm{CH{\cdot}CO_2Et} \\
| & \| \\
\mathrm{CH_2} & \mathrm{CH} \\
| & | \\
\mathrm{CH{\cdot}CO_2Et} & \mathrm{CH_2{\cdot}CO_2Et}
\end{array}$$

(Normal ester.) (Labile ester).

$$\begin{array}{ll}
\mathrm{CH_2{\cdot}CO_2Et} & \mathrm{CH_2{\cdot}CO_2H} \\
| & | \\
\mathrm{CH{\cdot}CH(CN){\cdot}CO_2Et} & \mathrm{CH{\cdot}CH_2{\cdot}CO_2H} \\
| & | \\
\mathrm{CH_2{\cdot}CO_2Et} & \mathrm{CH_2{\cdot}CO_2H}
\end{array}$$

(III.) (IV.)

238. "*The Chemistry of the Glutaconic Acid.* Part X. *The Alkylations of the Ethereal Salts.*" By Jocelyn Field Thorpe and Arthur Samuel Wood. (*Trans.*, 1913, 1752).

The formation of alkyl derivatives from esters of the glutaconic acids is controlled by the following generalisations:—

1. The formation of the sodium derivative of an ester of a glutaconic acid, and hence the formation of an alkyl

derivative, takes place through the labile form of the ester alone.

2. The normal esters, as such, do not react with sodium ethoxide.

3. The formation of a sodium derivative of a normal ester is therefore dependent on the tendency for the ester to pass into the labile modification under the experimental conditions employed.

4. The formation of a sodium derivative from a normal ester of a monoalkylated dicarboxylic acid involves the passage of the mobile hydrogen atom to the carbonyl system not affected by the substituting group. The second alkyl group therefore enters on the carbon atom of the three-carbon system most remote from that bearing the existing alkyl group.

5. Those esters which contain two or three potentially mobile hydrogen atoms can be made to yield dialkyl derivatives having the alkyl groups on the same carbon atom by alkylating them under conditions which prevent the passage of the labile monoalkyl derivative, which is first formed, into its normal isomeride. This can be effected by the presence of excess of sodium ethoxide throughout the alkylation.

6. Esters, although they may have the labile structure, will not react with sodium ethoxide if the nature of the groups carried by the carbon atoms of the three-carbon system is such as to prevent the movement of the hydrogen atom within the molecule.

239. "*The Formation and Reactions of Imino-compounds.* Part XVIII. *The Condensation of* cyclo*Hexanones with Cyanoacetamide Involving the Displacement of an Alkyl Group.*" By JOCELYN FIELD THORPE and ARTHUR SAMUEL WOOD. (*Trans.*, 1913, 1586).

Whereas 3-methyl*cyclo*hexanone and 4-methyl*cyclo*hexanone yield condensation products with cyanoacetamide from which 3-*methyl*cylo*hexane*-1 : 1-*diacetic acid* (I.) and 4-*methyl*cyclo*hexane*-1 : 1-*diacetic acid* (II.) can be prepared in large quantity, 2-methyl*cyclo*hexanone and 1 : 3-dimethyl*cyclo*hexane-4-one condense with the amide to form *cyclo*hexane-1 : 1 diacetic acid (III.) and 4-methyl-*cyclo*hexane-1 : 1-diacetic acid (II.) respectively.

$$CH_2<\begin{matrix}CHMe\cdot CH_2\\ CH_2-CH_2\end{matrix}>C<\begin{matrix}CH_2\cdot CO_2H\\ CH_2\cdot CO_2H\end{matrix}$$

(I.)

$$CHMe<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>C<\begin{matrix}CH_2\cdot CO_2H\\ CH_2\cdot CO_2H\end{matrix}$$

(II.)

$$CH_2<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>C<\begin{matrix}CH_2\cdot CO_2H\\ CH_2\cdot CO_2H\end{matrix}$$

(III.)

Since great care was taken to use these ketones in a very pure form, it follows that the presence of the methyl group in the 2-position inhibits condensation, but that the tendency for the formation of a condensation product is so considerable that it is effected through the displacement of this group, probably as methyl alcohol.

The by-products formed to the extent of about 10 per cent in the reactions between the ketones and cyanoacetamide are the cyano-imides (IV.) formed in accordance with the equation :—

$$\begin{matrix}CN\cdot CH_2\cdot CO\cdot NH_2\\ COR_2\\ CN\cdot CH_2\cdot CO\cdot NH_2\end{matrix} \rightarrow \begin{matrix}CN\cdot CH\cdot CO\\ |\\ CR_2\\ |\\ CN\cdot CH\cdot CO\end{matrix}\!\!>NH + H_2O + NH_3$$

(IV.)

240. "*The Replacement of Alkyl Groups in Tertiary Aromatic Bases.*" By JOCELYN FIELD THORPE and ARTHUR SAMUEL WOOD. (*Trans.*, 1913, 1601).

Experiments are described showing the unsuitability of the bases diethyl- and dimethyl aniline for the purpose of eliminating hydrogen haloid from substances capable of parting with these elements. It is shown, for example, that there is always a tendency for the base to combine with the halogen derivative, forming a quaternary salt, and that when once this salt is formed a decomposition represented by the equation—

$$\begin{matrix}Ph\cdot NR_2Br\\ |\\ CH_2R\cdot CH\cdot CO_2Et\end{matrix} \rightarrow \begin{matrix}Ph\cdot N\cdot R\\ |\\ CH_2R\cdot CH\cdot CO_2Et\end{matrix} + RBr$$

(Quaternary salt).

ensues on heating.

In the case of those substances which are not capable of eliminating hydrogen haloid, the formation of the quaternary salt and its decomposition in accordance with the equation—

$$\begin{matrix}Ph\cdot NR_2Br\\ |\\ CH_2CO_2Et\end{matrix} \rightarrow \begin{matrix}Ph\cdot N\cdot R\\ |\\ CH_2\cdot CO_2Et\end{matrix} + RBr$$

is quickly completed.

The reactions between the dialkylanilines and both trimethylene bromide and ethylene dibromide are also described.

241. "*Coumaranone Derivatives.* Part II. *The Constitution of Ethyl Coumaranonecarboxylate.*" By RICHARD WILLIAM MERRIMAN. (*Trans.*, 1913, 1838).

Several distinct observations indicate that ethyl coumaranonecarboxylate normally exists in the enolic form $C_6H_4<\begin{matrix}-O-\\ C(OH)\end{matrix}\!\!\geq C\cdot CO_2Et$. (*a*) During many subsequent attempts to prepare the phenylhydrazone described in Part I. (*Trans.*, 1911, xcix., 911) an isomeric substance, $C_6H_4<\begin{matrix}O\\ C(NH\cdot NHPh)\end{matrix}\!\!\geq C\cdot CO_2Et$, was always obtained. (*b*) An oxime could not be isolated. (*c*) Exactly one equivalent of sodium hydroxide was required to neutralise the ester. (*d*) It reacts towards Grignard's reagent entirely in the enolic form. (*e*) The absorption curves of the ester and its acetyl derivative are practically identical. The addition of alkali completely alters the character of the absorption spectrum. This fact has been explained by the modification of Hantzsch's theory proposed by Brannigan, Macbeth, and Stewart (*Trans.*, 1913, ciii., 415).

o-*Carbamylphenoxyacetic acid*,—

$$NH_2\cdot CO\cdot C_6H_4\cdot O\cdot CH_2\cdot CO_2H,$$

was prepared during this investigation.

242. "*Coumaranone Derivatives.* Part III. *Acylazo-derivatives of Coumaranonecarboxylic Acid.*" By RICHARD WILLIAM MERRIMAN. (*Trans.*, 1913, 1845).

Benzeneazocarbonylcoumaranone,—

$$C_6H_4<\begin{matrix}-O-\\ C(OH)\end{matrix}\!\!\geq C\cdot CO\cdot N:NPh,$$

and its phenyl hydrazone,—

$$C_6H_4<\begin{matrix}O\\ C(:N\cdot NHPH)\end{matrix}\!\!>CH\cdot CO\cdot N:NPh$$

(Part I., *Trans.*, 1911, xcix., 911), have been subjected to further investigation, the results of which confirm the formulæ assigned to them.

An acetate and metallic derivatives of benzeneazo-carbonylcoumaranone have been prepared. By reducing an alkaline solution of the orange azo-compound with zinc dust the colourless hydrazo-derivative,—

$$C_6H_4<\begin{matrix}O\\ CO\end{matrix}>CH\cdot CO\cdot NH\cdot NHPh,$$

was obtained. When stannous chloride or sodium hyposulphite was used as the reducing agent, the azo-group was broken, with the liberation of aniline.

The red azophenylhydrazone also forms an acetate and metallic derivatives. This phenylhydrazone is extremely resistant towards all hydrolytic agents, except fuming hydrobromic acid, which converts it into the parent azo-compound.

Similar colourless hydrazo-compounds, orange azo-

compounds, and red hydrazones of the latter have been prepared by using the three tolylhydrazines in place of phenylhydrazine.

The absorption spectra of the above compounds have been measured and compared with those of s-benzoylphenylhydrazine, NHBz·NHPh, and Fischer's benzoylazobenzene, NBz:NPh.

243. "*The Dynamics of Bleaching.*" By SYDNEY HERBERT HIGGINS. (*Trans.*, 1913, 1816).

Experiments on the bleaching of linen cloth containing a large excess of colouring matter, by means of very dilute bleaching powder solution, show that the bleaching action proceeds in accordance with the equation $HOCl = HCl + O$, and is thus a unimolecular reaction.

The influence of adding lime-water or hydrochloric acid to the bleaching solution was also studied.

(To be continued).

INSTITUTE OF CHEMISTRY.

At a meeting of the Institute of Chemistry held at the Imperial College of Science and Technology, South Kensington, on Wednesday, November 26, the second lecture on "*The Research Chemist in the Works, with Special Reference to the Textile Industry*" was delivered by Mr. W. P. Dreaper, F.I.C. Dr. George McGowan, Vice-President, in the Chair.

Continuing his subject, the lecturer called attention to the importance of a knowledge of theory, and illustrated this point specially by a reference to the work done in connection with the presence of stains and loss of strength experienced on the storage of certain silk goods. This was found to be due to the free sulphuric acid. Only a knowledge of theory had suggested why this could be present in cases where this acid had never been used in any process of manufacture. The so-called "neutral salt reaction" had offered a solution to this problem, and has relieved the dyer from constant blame.

The British aniline dye industry had recently made remarkable progress, and its products were even being sold in Germany. The future would see considerable expansion in this reviving industry.

The work of the textile chemist was further illustrated by reference to the manufacture of crêpe de chine, and the part played by the chemist in the production of the "crape" effect, and its retention through subsequent processes of manufacture.

Dealing generally with the subject of embossing, attention was drawn to the evolution of what was known as mourning crape, with its extremely complicated process of manufacture. Some fifty years ago a Tottenham weaver attempted to improve upon the product as then imported from China, which was of the nature of a rough silk material. This weaver attempted to make it more realistic by representing on its surface "the tears of the mourners." This was accomplished by passing the cloth and a long length of fishing net through a pair of rollers. This original design can be detected upon the modern products, although in almost every other respect the manufacture has changed. Under modern conditions the chemist is required to direct every step from the raw material to the final waterproofing process.

The processes of bleaching cotton, as used to-day, were then described and illustrated by samples, and the principles involved in dyeing, finishing, and printing fabrics were touched on.

When the chemist produced results in the laboratory and desired to see them reproduced on a large scale, it was essential that he should be in a position to indicate to the engineer the nature of the machinery required; better still, to submit a design for the same. The method of attack adopted by the chemist was so essentially different, in its direction and nature, from that adopted by the engineer that this alone justified his presence in any works. It also defined the relative position of the chemist and engineer; it was sometimes necessary for the chemist to retain control of certain industrial processes which had emanated from the laboratory, especially when these were more dependent upon chemical factors than mechanical or electrical ones; thus the chemist became directly involved in working conditions and industrial operations.

The influence of the chemist on the choice of raw materials should be greatly extended. This point had received attention in certain quarters. The South African Government still recommended the use of a sheep-dip which seriously reduced the value of South African wool and gave great trouble in subsequent manufacture. This matter had been repeatedly brought to their notice.

In conclusion, it was pointed out that a rigidly chemical training was an insufficient equipment for the modern investigator. He would either find himself working over long periods in other directions, or failing to follow up investigations just when they became interesting and profitable. Given a suitable subject almost everything depended upon attention to detail.

For the right man properly trained the textile industry offered a good opening, when the worker concerned himself with problems of general interest rather than with factory detail, the matching of colours, and the like. Many chemists wasted their early years of research on matters which, although important in themselves, led nowhere. This should be avoided whenever possible.

The lecture was illustratad by examples of machinery used, samples of textile materials in the intermediate stages of manufacture, and actual demonstrations of hand, block, and spray printing.

CORRESPONDENCE.

GALLIUM: ITS WIDE DISTRIBUTION, &c.

To the Editor of the Chemical News.

Sir,—Two French chemists have recently observed the presence of gallium in commercial aluminium, and it has been announced as a new discovery (Boulanger and Bardet, Academy of Sciences, October, 27, 1913; Chem. News, cviii., 232). I feel it is necessary to call attention to the fact that the presence of gallium in aluminium was first observed by the late Prof. Sir Walter N. Hartley and myself as far back as 1897 (*Trans. Chem. Soc.*, 1897, p. 547).

It may interest Mr. F. H. Loring (Chem. News, cviii. 247) to know that during the years 1895—9, the presence of gallium was also discovered in iron, in many iron ores, in siderite, aluminous minerals, manganese ores, very many silicates and other minerals, in dust from various sources, &c., and in meteorites, and its presence in the sun was also established. It is, in fact, one of the most widely distributed elements, but in no case has it been discovered in large quantity.

I have recently, after an interval of nearly ten years in which research has been practically impossible, begun a search for the richest source of gallium.—I am, &c.,

Hugh Ramage.

Technical Institute, Norwich.

THE NEW AMERICAN DUTY TARIFF.

To the Editor of the Chemical News.

Sir,—As we are still receiving enquiries from manufacturers and others, it is evident that many business houses are still unfamiliar with the duties now payable on the goods in which they are concerned.

It may interest your readers to know that we still have a certain number of copies left, and we would be very pleased to supply these free of charge for such time as our stock lasts.—We are, &c.,

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NOTICES OF BOOKS.

Outlines of Mineralogy. By GREVILLE A. J. COLE. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1913.

THIS book is intended chiefly for students of geology, and will serve them excellently as an introductory course in mineralogy. The characters of minerals are described in Part I., which contains a short outline of the principles of crystallography and also a clear account of methods of investigating the optical characters of minerals. In the second part of the book the minerals are first classified as ores of the elements arranged according to the periodic system, and then comparatively full data are given of the individual minerals.

A Treatise on Quantitative Inorganic Analysis with Special Reference to the Analysis of Clays, Silicates, and Related Minerals. Vol. I. By J. W. MELLOR, D.Sc. London: Charles Griffin and Co., Ltd. 1913.

THOSE chemists who are specially interested in the analysis of the materials employed in the ceramic industries should not fail to get a copy of this work, which will at once take its place in scientific literature as the standard work on the subject. The author's experience in the Testing Department of the County Pottery Laboratory, Staffordshire, has given him unique opportunities of testing different methods and working out schemes for the analysis of silicates, &c., and many of the processes described have been employed for years, after having been modified in accordance with the experience of students in the analytical classes and of the professional staff. The author has also kept pace with the ever-growing mass of literature on the subject, and in extensive footnotes gives an enormous number of references to English and foreign periodicals. He writes in a graphic style, and is a great believer in the value of paying attention to the smallest details. The causes of faulty results in analytical work and want of agreement between the results of different workers are very helpfully discussed.

Quantitative Analysis in Practice. By JOHN WADDELL, B.A. (Dalhousie University), B.Sc. (London), Ph.D. (Heidelberg), D.Sc. (Edinburgh). London: J. and A. Churchill. 1913.

THE methods described in this text-book of quantitative analysis have been selected as being suitable for the elementary work both of technical students and of those who are intending to devote themselves to the pure science. They include some gravimetric methods for common metals and acid radicles, such as Ba, Mg, Cl, SO_4, and also the analysis of complex substances, such as limestones, clays, &c. The electrolytic determination of copper is described, as well as some volumetric methods and their applications to certain ores. The author lays great stress upon the need for forethought and economy of time, and the actual times necessary for each analysis and in some cases for the separate steps of it are stated. Thus, although accuracy is given first place as the aim which should be pre-eminent in the student's mind, he is kept up to the mark as regards speed, and the book will provide a specially good training for technical analysts.

The Chemical Trade. *Pitman's Specialised Correspondence Books*. London, Bath, and New York: Sir Isaac Pitman and Sons, Ltd.

THIS little book will provide the shorthand writer or typist who is in a chemist's office with a certain amount of material by means of which he can make himself acquainted with the terms, &c., employed in the business. It contains more than forty letters and market reports dealing with the chemical industries, marked off in twenties for the purposes of dictation, and if the shorthand typist studies them carefully and follows the editor's advice regarding the setting out of statistical matter on a typewriter, the working out of calculations involving the English and metric systems and similar details, he will increase his efficiency and add to his chance of promotion to a more responsible position. It is pointed out that a knowledge of the science is most valuable, to enable him to correct errors on the part of his employer, and he is given, perhaps unintentionally, at least one chance of performing the same office for his text-book.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances des l'Academie des Sciences. Vol. clvii., No. 16, October 20, 1913.

This number contains no chemical matter.

Berichte der Deutschen Chemischen Gesellschaft. Vol. xlvi., No. 12, 1913.

Titrimetric Determination of Fluorine.—Alfred Greeff.—A solution of ferric chloride produces a white crystalline precipitate of general formula $[FeF_6]X_3$ in neutral aqueous solutions of alkali fluorides. Sodium iron fluoride is only very slightly soluble in water, and does not give the characteristic red colouration with sulphocyanides. To determine fluorine 0·5 grm. of the substance are dissolved in 25 cc. of hot water, about 25 grms. of sodium chloride are added to the cooled solution, and about 5 cc. of sulphocyanide solution. The solution is then titrated with iron chloride solution till it becomes pale yellow. Ten cc. of alcohol and 10 cc. of ether are added, and more iron chloride solution is carefully run in until after shaking and allowing to stand the red colouration still persists. Every molecule of $FeCl_3$ used corresponds to six molecules of NaF. The solution of fluoride used must be neutral to phenolphthalein. Solutions of sodium silicofluoride or of acid sodium fluoride must first be treated with caustic soda, when the neutral fluoride will be obtained:—

$$Na_2SiF_6 + 4NaOH = 6NaF + SiO_2 + 2H_2O,$$
$$NaF.HF + NaOH = 2NaF + H_2O.$$

Action of Sulphur Trioxide on Salts.—Wilhelm Traube.—When sodium chloride is subjected to the action of sulphur trioxide the product is the sodium salt of chlorpyrosulphonic acid, $NaCl + 2SO_3 = \begin{matrix} O_2.S.ONa \\ >O \\ O_2.S.Cl \end{matrix}$

Sodium chlorsulphonate, $NaClSO_3$, is undoubtedly formed as an intermediate product. Sodium fluoride gives with sulphur trioxide addition products, which are quite different from those obtained from the chlorides. Their aqueous solutions are neutral, and they do not give the reactions of either hydrofluoric or sulphuric acids. These salts are derived from fluosulphonic acid. Nitrites absorb SO_3, giving salts of nitrosotrisulphonic acid, *e.g.*, $NO_2(SO_3)_3Na$, and persulphates behave similarly, the products being probably perpyrosulphates, $K_2S_2O_8 + 2SO_3 = KS_2O_6.O_2.S_2O_6K$.

Aromatic Compounds containing Selenium.—R. Lesser and R. Weiss.—When thionyl chloride or phosphorus pentachloride acts on diphenyl diselenide, di-*o*-carboxylic acid, besides the chloride, an addition produc of formula $\left(\begin{matrix}H\\Cl\end{matrix}{>}Se.C_6H_4.CO.Cl\right)_2$, is obtained. This indicates that the group Se.Se possesses very strongly basic properties and is capable of forming salts. The authors have prepared a series of indigoid dyes derived from 3-oxyselenonaphthene, and also a number of condensation products of the latter, chiefly with aldehydes.

Cerium Dioxide as Contact Substance in Organic Combustions.—Julius Bekk.—Cerium dioxide acts as a catalyst in the combustion of gases, and it can conveniently be used in quantitative experiments by Dennstedt's method. Asbestos impregnated with the oxide is prepared by soaking pure asbestos in a concentrated solution of cerous nitrate and then igniting.

Separation of Halogen Hydride by Phosphorus Pentoxide.—H. Lecher.—Phosphorus pentoxide acts energetically as a catalyst in the separation of halogen hydrides. Thus, if benzoyl chloride is warmed with excess of naphthalene no reaction occurs, but if a small quantity of phosphorus pentoxide is added, HCl is at once evolved, and a 90 per cent yield of α- and β-naphthyl phenyl ketone is obtained. Only small quantities of the catalyst are needed and large amounts have an unfavourable effect. One drawback of the new catalyst is the high temperature at which the reactions occur.

Atomic Weight of Yttrium.—R. J. Meyer and M. Weinheber.—The authors have carried out a new series of atomic weight determinations as follows:—They dissolved the oxide in a little nitric acid in a platinum dish, added rather more than the calculated amount of sulphuric acid, and evaporated to crystallisation. The octohydrate, $Y_2(SO_4)_3+8H_2O$, then separated in clear monoclinic crystals. The mother-liquor was then poured off and the crystals washed with ice-water and then dehydrated by heating to 300—400°. The anhydride thus obtained was dissolved in water and the solution evaporated. This operation was repeated twice. The crystalline salt thus obtained is quite neutral. Some of it was weighed in a platinum crucible and heated to 400° in an electric furnace, and thus dehydrated to constant weight. The sulphate was then converted into oxide by heating before the blowpipe. The results thus obtained agree very well, and the most probable value of the atomic weight is 88·7.

Oxidation of Coals at Moderate Temperatures.—K. A. Hofmann, K. Schumpelt, and K. Ritter.—The authors have already reported that amorphous coal is oxidised by chlorate solutions, made active by means of osmium tetroxide, at the temperature of the water-bath, the products being carbon dioxide, mellogen, and mellitic acid. In further experiments they have now found that carbon is much more readily oxidised at moderate temperatures than has been supposed. Thus a dilute aqueous solution of calcium hypochlorite acts energetically on it, the products being carbon monoxide and dioxide. Amorphous carbon in presence of alkalis at 120—150° gives dark brown and red colloids, and then yields formate and oxalate, and finally carbonate.

Preparation of Pure Anhydrous Selenium Dioxide, and the Atomic Weight of Selenium.—Josef Jannek and Julius Meyer.—Selenium dioxide can readily be oxidised by a mixture of N_2O_4 and oxygen, and no trace of the hypothetical SeO_3 nor of the acid is formed. The N_2O_4 acts simply as a carrier of oxygen, as in the lead chamber process. Between 400° and 500° SeO_2 can be sublimed unchanged, but at higher temperatures it is decomposed. This method of oxidising selenium provides a convenient process for determining the atomic weight of selenium. The results obtained are Se=79·158 in air and Se=79·141 *in vacuo*.

MISCELLANEOUS.

Royal Institution.—A General Meeting of the Members of the Royal Institution was held on the 1st inst.; the Duke of Northumberland, President, in the Chair. Mr. Howard Marryat and Mr. H. Gordon Selfridge were elected Members, and Dr. Henri Deslandres (Paris) was elected an Honorary Member of the Institution. The Chairman announced the decease of Sir William Preece, a Member of the Institution, and a resolution of condolence with the family was passed.

Royal Institution.—The following are the lecture arrangements at the Royal Institution, before Easter:—Prof. H. H. Turner, Savilian Professor of Astronomy, Oxford, a course of experimentally illustrated lectures, adapted to a juvenile auditory, on "A Voyage in Space: The Starting Point—Our Earth," December 27; "The Start through the Air," December 30; "Journeying by Telescope," January 1; "Visits to the Moon and Planets," January 3; "Our Sun," January 6; "The Stars," January 8. Prof. W. Bateson, Fullerian Professor of Physiology, Royal Institution, six lectures on "Animals and Plants under Domestication." Prof. Sir John H. Biles, three lectures on "Modern Shipbuilding—(1) Smooth Water Sailing; (2) Ocean Travel; (3) The War Navy." Mr. Arthur H. Smith, two lectures on "Landscape and Natural Objects in Classical Art." Dr. W. McDougall, two lectures on "The Mind of Savage Man (Illustrated by the Pagan Tribes of Borneo—(1) His Intellectual Life; (2) His Moral and Religious Life." Prof. Sir Thomas H. Holland, two lectures on "Petroleum Supply from the Geological Point of View." Prof. I. Gollancz, two lectures on "Hamlet in Legend and Drama—(1) The Myth; (2) The Play." Prof. C. F. Jenkin, three lectures on "Heat and Cold." Dr. C. W. Saleeby, two lectures on "The Progress of Eugenics—(1) The First Decade of Modern Eugenics, 1904—14; (2) Eugenics To-day—Its Counterfeits, Powers, and Problems." Prof. F. Corder, three lectures on "Neglected Musical Composers—(1) Ludwig Spohr; (2) Henry Bishop; (3) Joachim Raff" (with Musical Illustrations). Dr. J. A. Harker, two lectures on "The Electric Emissivity of Matter—(1) The Metals; (2) Other Substances" (with Experimental Illustrations). Prof. Sir J. J. Thomson, Professor of Natural Philosophy, Royal Institution, six lectures on "Recent Discoveries in Physical Science." The Friday Evening Meetings will commence on January 23, when Prof. Sir James Dewar will deliver a Discourse on "The Coming of Age of the 'Vacuum Flask.'" Succeeding Discourses will probably be given by Mr. H. Wickham Steed, Dr. H. S. Hele Shaw, Prof. J. Norman Collie, Prof. W. A. Bone, Rev. Canon J. O. Hannay ("George A. Birmingham"), Sir Walter R. Lawrence, Bart., the Right Hon. Lord Rayleigh, Prof. J. A. Fleming, Prof. Sir J. J. Thomson, Dr. A. Keith, and other gentlemen.

MEETINGS FOR THE WEEK.

Monday, 8th.—Royal Society of Arts, 8. (Cantor Lecture). "The Measurement of Stresses in Materials and Structures," by Prof. E. G. Coker, D.Sc.

Tuesday, 9th.—Biochemical Society, 5.30. (At the Lister Institute, Chelsea Gardens, S.W.).

Wednesday, 10th.—Royal Society of Arts, 8. "Applications of Electricity to Agriculture and Life," by T. Thorne Baker.

Thursday, 11th.—Royal Society. "Intermittent Vision," by A. Mallock. "Relations between the Crystal Symmetry of the Simpler Organic Compounds and their Molecular Constitution," by W. Wahl. "Selective Absorption of Ketones," by G. G. Henderson and J. M. Heilbron. "Absolute Measurements of a Resistance by a Method based on that of Lorenz," by F. E. Smith. "Determination of the Electromotive Force of the Weston Normal Cell in Semi-absolute Volts," by A. N. Shaw. "Elastic Hysteresis in Steel," by F. E. Rowett. "Simple Form of Micro-balance for Determining the Densities of Small Quantities of Gases," by F. W. Aston. "A Second Spectrum of Neon," by T. R. Merton.

Friday, 12th.—Alchemical Society, 8.15. (At International Club, Regent Street, S.W.). "Alchemy in China," by Prof. H. Chatley, B.Sc.

THE CHEMICAL NEWS.

VOL. CVIII., No. 2820.

ANODIC AND CATHODIC RETARDATION PHENOMENA AND THEIR BEARING UPON THE THEORY OF PASSIVITY.*

By G. GRUBE (Dresden).

(Concluded from p. 273).

A SYSTEMATIC investigation by F. Foerster and J. Yamasaki (*Zeit. Elektrochem.*, 1910, xvi., 321) of the phenomena which accompany the discharge of bromine from neutral and alkaline potassium bromide solutions, had established that the anodic discharge of bromine ions from platinised platinum anodes was only then reversible, when the anode in question was free from any oxygen charge. When, however, the anode was charged with oxygen, be that by anodic polarisation or by a liberation of oxygen during the electrolysis of the bromide, the discharge of the bromine took place at potentials considerably more noble than those one might have expected for the reversible reaction from the observed bromine potentials. Thus an oxygen content of the platinised electrode retards the discharge of the bromine ions.

Quite recently F. Foerster and F. Herrschel (F. Herrschel, "Dissertation," Leipzig, 1912) have also studied

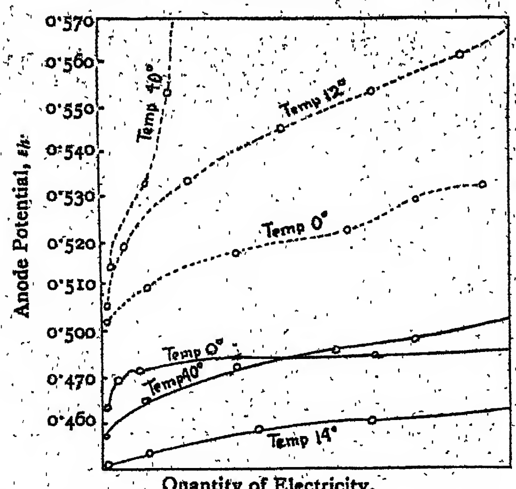


FIG. 5.

the retardation of the iodine discharge from iodide solutions. The electrolysis of neutral and of alkaline solutions of potassium iodide, it resulted, did not in general prove strictly reversible. The anode showed temporarily increasing polarisations, much more intense than concentration effects, and this temporary rise of the potential was much greater with smooth platinum anodes than with platinised anodes. The increase further grew with rising temperature and increasing current density. The polarisation was further more marked when the concentration ratio C_{OH}'/Cz' of the alkaline solution was increased.

The temperature influence upon the anode potential, as well as the difference in the potentials with smooth and with platinised platinum, can be seen from Fig. 5. The anode potentials are plotted against the electricity quantities expended, measured with a current intensity of 1 ampère and with smooth and platinised platinum at different temperatures in a solution which was normal as to KI and 0·9 normal as to iodine. The full curves refer to platinised platinum, the dotted curves to smooth platinum. We see that the polarisation is much stronger with the smooth platinum, and further that a rise of temperature calls forth a material increase in the polarisation. That the marked temporary rise in the polarisation, also with the iodine discharge, was indeed due to an oxygen charge on the anode, was proved by the comparison between the polarisation of a cathodically pre polarised platinised electrode free from oxygen and the polarisation of an anodically polarised electrode charged with oxygen. The result of one of these experiments, performed with a solution normal as to KI, 0·9 normal as to iodine, at ordinary temperature, is reproduced in Fig. 6. We see at once how great the increase in the polarisation is which has been produced by charging the anode with oxygen.

The experiments alluded to leave no more doubt that the retardations, which occur when bromine and iodine are discharged from neutral or alkaline solutions of bromide or iodide, are to be traced back to an oxygen charge on the anode. When looking for an explanation of this interesting phenomenon we shall first have to consider the process of the oxygen evolution carefully. This evolution, it has long been known, does not represent a reversible process. Whilst we should expect the evolution to take

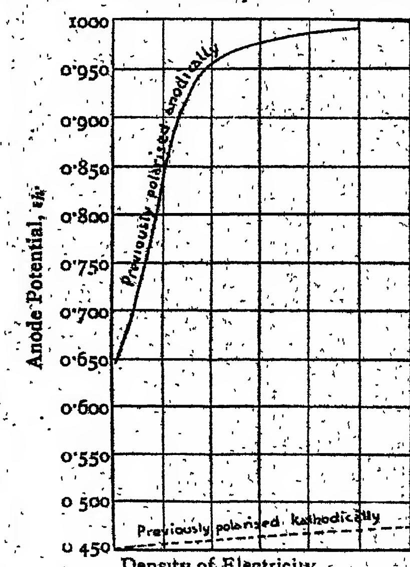


FIG. 6.

place in $2N-H_2SO$ at a potential $_{\epsilon h} = +1·23$ volt, it is so much retarded that, at a platinised anode, it does not set in before $_{\epsilon h} = +1·5$ volt, and the potentials have further to be raised when the evolution is continued. Thus the oxygen evolution shows, like the discharge of the halogens, a temporary strong rise of the polarisation value. To understand this retardation of the anodic oxygen liberation we must assume, following F. Foerster's theory (*Zeit. Phys. Chem.*, 1909, lxix., 236), that the potential of the electrode depends upon the anodically discharged oxygen which forms an unstable primary oxide, PtO_x, with the platinum. This oxide is soluble in the finely distributed platinum of the platinised electrode, and passes, under evolution of oxygen, into a more stable lower oxide, PtO perhaps. The latter is again soluble in the finely distributed platinum. We have now to assume that the rate of decomposition of the primary oxide is diminished in the same measure as

* Communication from the Laboratory for Physical Chemistry and Electrochemistry of the Technical High School, Dresden. (Translated from the German). Contribution to the General Discussion on "The Passivity of Metals" held before the Faraday Society, Nov. 12, 1913.

he concentration of the stable oxide on the surface of the electrode increases. In order then to maintain a constant current density, *i.e.*, in order always to evolve the same amount of oxygen, the concentration of the primary oxide, and therefore the anode potential, should increase together with increasing formation of the stable oxide on the surface of the electrode. I have been able to demonstrate (G. Grube, *Zeit. Elektrochem.*, 1910, xvi., 621), by comparative potential measurements of the platinum oxides and of platinised platinum electrodes (after polarisation in sulphuric acid), that the anodic evolution of oxygen from platinised electrodes, so far as it takes place below the anode potential $_{\epsilon}h = +1\cdot6$ volt, is connected with the formation and decomposition of the platinum trioxide, so that PtO_3 would agree with PtO_x. For still higher potentials, observed at platinised electrodes, we must, in order to account for the oxygen evolution, presume the intermediation of a still higher oxide, possibly PtO_4.

After our having thus experimentally demonstrated that the retardation of the anodic oxygen evolution can satisfactorily be explained by the existence of unstable platinum oxides, it would appear plausible that the retarded halogen discharge from platinum electrodes could be accounted for by the aid of intermediate compounds similar to the primary oxides of platinum. Luther and Brislee (*loc. cit.*) already supposed that the discharge of chlorine from smooth platinum might be secondary, via some unknown intermediate product lying between Cl' and Cl_2. If we accept the existence of such a product, by ascribing to platinum a certain solubility for discharged halogen ions, we might imagine that the decomposition of unstable products (which are characteristic for the status nascendi of the halogens) might be impeded by an oxygen charge on the anode in a similar way as we assumed for the decomposition of the primary oxides of platinum (characteristic for the status nascendi of oxygen).

When we review the researches which we have been discussing with regard to their bearing on the theory of passivity, the following main points should be accentuated :—

1. It has been proved that the cathodic deposition of the iron metals—in itself a slowly-progressing reaction—can still more be retarded to a considerable extent by the simultaneous deposition of zinc or of hydrogen. The cause of these retardations is probably to be found in a change of the surface of the electrode, the change being characterised by the formation of unstable intermediate products of higher electrolytic solution pressure than the pure metals possess.

2. The circumstance that cathodic processes can materially be retarded by the occurrence of small quantities of foreign substances on the electrode lends essential support to the assumption that anodic processes may likewise be retarded by the formation of oxygen alloys on the anodes. In many cases therefore the cause of the anodic passivity will not be a mechanical closure (covering up) of the electrode surface by an oxide film, but the formation of an alloy consisting of the material of the anode surface and of oxygen, this alloy having a lower electrolytic solution pressure than the pure metal.

3. In the electrolytic oxidation of ferropotassium cyanide to ferripotassium cyanide a strong polarisation was always observed when the electrodes were surrounded by films of ferrocyanide or of oxides. These strong polarisations were not found with platinum, gold, nickel, cobalt, and copper in alkaline solutions. It may therefore be concluded that, in this latter case, the passivity is caused, not by an oxide film, but by an oxygen alloy on the anode.

4. It has been shown that the retardations observed in the anodic discharge of the halogens are likewise to be ascribed to alloys of the platinum anodes with oxygen.

5. It has been exemplified by the anodic evolution of oxygen what we have to understand by the passivating oxygen alloys. We may imagine that the oxygen combines to a small extent with the anode material to form oxides, which in their turn form, together with the unchanged electrode material, solid solutions, and therefore one-phase systems of continuously variable composition and likewise variable electrolytic solution pressure. The oxide-film theory contrasts with this view, since according to that theory the oxide formed would mechanically cover and shut off the electrode surface so that oxide-film and electrode would form a two-phase system. The oxygen-alloy theory of the passivity thus seeks the cause of the passivity in a change of the chemical properties of the anode material, whilst the oxide-film theory finds the cause in a change of the mechanical properties of the electrode surface.

THE AMMONIA SYSTEM OF ACIDS, BASES, AND SALTS.*

By EDWARD C. FRANKLIN.

(Continued from p. 274).

III. *Acids, Bases, and Salts of the Ammonia System.*

4. *Compounds Related to Ammonia as the Ordinary Oxygen Acids, Bases, and Salts are Related to Water.*—A consideration of the many points of resemblance between water and liquid ammonia as electrolytic solvents has led the writer to the conception of a system of acids, bases, and salts in which ammonia occupies a position similar to that held by water in its relation to the ordinary oxygen acids, bases, and salts. The compounds bearing such a relationship to ammonia are the acid amides and imides, the metallic amides and imides, and the metallic derivatives of the acid amides and imides respectively. Just as acetic acid, for example, may be looked upon as a derivative of water in which one-half of the hydrogen is replaced by the electronegative radical, acetyl, so acetamide is ammonia in which one-third of the hydrogen is replaced by acetyl; as potassium hydroxide is a derivative of water, so is potassium amide a similar derivative of ammonia; and in the same sense that potassium acetate is derived from water, so potassium acetamide may be regarded as ammonia in which a part of the hydrogen is replaced by potassium and another part by the acetyl group. Finally, the familiar relations existing between the metallic hydroxides and oxides and between acids and acid anhydrides are exemplified, at least formally, in the analogous relationship which the metallic amides and imides, on the one hand, bear to the metallic nitrides, and which the acid amides and imides, on the other hand, bear to the non-metallic nitrides.

5. *Nomenclature.*—The ordinary acids, bases, and salts, which were first recognised by Lavoisier as being oxygen compounds, came later to be looked upon as derivatives of water, and as such constituting what may be called a water system of acids, bases, and salts. Under the influence of the dictum of Lavoisier that oxygen is a never-failing constituent of all acids, chemists assumed that hydrochloric acid, the one known halogen acid, was a hydrated oxide of an unknown element; and it was only after the demonstration of the elementary nature of iodine and chlorine that a class of oxygen-free acids and salts—the halogen acids and salts—came to be clearly recognised. Latterly a limited number of other oxygen-free compounds have come to be recognised as possessing the properties of acids, bases, and salts, conspicuous among them being the sulpho acids, bases, and salts. Certain acid amides have long been known to possess acid properties to the extent, at least, of forming salt-like metallic derivatives, but it is only since the investigations of the writer and his collaborators have demonstrated the acid, basic, and salt-like character of the acid amides, the metallic amides, and the metallic derivatives of the acid amides respectively, that the existence of an ammonia system of acids, bases, and salts must be recognised.

* From *American Chemical Journal*, xlvii., No. 4.

I.

The Water or Oxygen System.		The Ammonia or Nitrogen System.	
Aquo Acids and Acid Anhydrides.		*Ammono Acids and Acid Nitrides.*	
Acetic acid	CH_3COOH	Acetamide	CH_3CONH_2
		Diacetamide	$(CH_3CO)_2NH$
Acetic anhydride	$(CH_3CO)_2O$	Triacetamide	$(CH_3CO)_3N$
Benzoic acid	C_6H_5COOH	Benzamide	$C_6H_5CONH_2$
Benzenesulphonic acid	$C_6H_5SO_2OH$	Benzenesulphonamide	$C_6H_5SO_2NH_2$
Nitrobenzenesulphonic acid	$C_6H_4(NO_2)SO_2OH$	Nitrobenzenesulphonamide	$C_6H_4(NO_2)SO_2NH_2$
Nitric acid	NO_2OH	Nitramide	NO_2NH_2
Sulphuric acid	$SO_2(OH)_2$	Sulphamide	$SO_2(NH_2)_2$
		Sulphimide	$(SO_2NH)_3$
Carbonic acid	$CO(OH)_2$	Carbamide	$CO(NH_2)_2$
		Nitrourea	$NH_2CONH(NO_2)$
		Guanidine	$HNC(NH_2)_2$
		Nitroguanidine	$NH_2C(NH)NHNO_2$
		Parabanic acid	$C_3O_3(NH)_2$
		Uric acid	$C_5O_3(NH)_4$
Cyanic acid	$CNOH$	Cyanoamide	$CNNH_2$
Picric acid	$C_6H_2(NO_2)_3OH$	Picramide	$C_6H_2(NO_2)_3NH_2$
Orthosilicic acid	$Si(OH)_4$	Silicon amide	$Si(NH_2)_4$
		Silicon imide	$Si(NH)_2$
Silicic anhydride	SiO_2	Silicon nitride	Si_3N_4

II.

Aquo Bases and Basic Oxides.		*Ammono Bases and Basic Nitrides.*	
Sodium hydroxide	$NaOH$	Sodium amide	$NaNH_2$
Lithium hydroxide	$LiOH$	Lithium amide	$LiNH_2$
		Lithium imide	Li_2NH
Lithium oxide	Li_2O	Lithium nitride	Li_3N
Calcium hydroxide	$Ca(OH)_2$	Calcium amide	$Ca(NH_2)_2$
Magnesium oxide	MgO	Magnesium nitride	Mg_3N_2
Mercuric oxide	HgO	Mercuric nitride	Hg_3N_2
Bismuth oxide	Bi_2O_3	Bismuth nitride	BiN

III.

Aquo Salts.		*Ammono Salts.*	
Potassium acetate	CH_3COOK	Monopotassium acetamide	CH_3CONHK
		Dipotassium acetamide	CH_3CONK_2
		Sodium diacetamide	$(CH_3CO)_2NNa$
Magnesium acetate	$(CH_3COO)_2Mg$	Magnesium acetamide	$(CH_3CONH)_2Mg$
		Monopotassium benzenesulphonamide	$C_6H_5SO_2NHK$
Potassium benzenesulphonate	$C_6H_5SO_2OK$	Dipotassium benzenesulphonamide	$C_6H_5SO_2NK_2$
Potassium sulphate	$KOSO_2OK$		
Potassium acid sulphate	$HOSO_2OK$	Dipotassium sulphamide	$KHNSO_2NHK$
		Monopotassium sulphamide	H_2NSO_2NHK
Potassium carbonate	$KOCOOK$		
Potassium acid carbonate	$HOCOOK$	Dipotassium urea	$KHNCONHK$
		Monopotassium urea	$H_2NCONHK$
		Potassium nitrourea	$H_2NCONKNO_2$
		Potassium nitroguanidine	$H_2NC(NH)NKNO_2$
Mercuric succinate	$\left.\begin{array}{l}CH_2COO\\ \mid\\ CH_2COO\end{array}\right>Hg$	Mercuric succinamide	$\left.\begin{array}{l}CH_2CONH\\ \mid\\ CH_2CONH\end{array}\right>Hg$
		Mercuric succinimide	$\left.\begin{array}{l}CH_2CO\\ \mid\\ CH_2CO\end{array}\right>NHg$
		Silver succinimide	$\left.\begin{array}{l}CH_2CNH\\ \mid\\ CH_2CNH\end{array}\right>NAg$
Isatin silver (Peters, *Ber.*, 1907, xl., 235)	$C_6H_4\left<\begin{array}{c}CO\\ N\end{array}\right>COAg$	Isatin mercury (Peters, *Ber.*, 1907, xl., 235)	$C_6H_4\left<\begin{array}{c}CO\\ NHg\end{array}\right>CO$
		Potassium parabanate	$C_3O_3(NH)(NK)$
		Calcium cyanoamide	$CNNCa$
Mercury cyanurate (Hantzsch, *Ber.*, 1902, xxxv., 2717)	$(CN)_3(OHg)_3$	Mercuric isocyanurate (Hantzsch, *Ber.*, 1902, xxxv., 2717)	$(CO)_3(NHg)_3$

IV.

Amphoteric Hydroxides.		*Amphoteric Amides, Imides, and Nitrides.*	
Zinc hydroxide	$Zn(OH)_2$	Zinc amide	$Zn(NH_2)_2$
		Silver amide	$AgNH_2$
Lead hydroxide	$Pb(OH)_2$	Lead imide	$PbNH$
		Cuprous nitride	Cu_3N
		Thallium nitride	Tl_3N

The Water or Oxygen System.		The Ammonia or Nitrogen System.	
V.			
Salts of Amphoteric Hydroxides.		*Salts of Amphoteric Amides and Imides.*	
Potassium zincate	—	Potassium ammonozincate	$KHNZnNKH.2NH_3$
Potassium plumbite	—	Potassium ammonoplumbite	$PbNK.2\frac{1}{4}NH_3$
Potassium stannate	$KOSnOOK.3H_2O$	Potassium ammonostannate	$KNSnNK.4NH_3$ or $K_2Sn(NH)_3.3NH_3$
VI.			
Aquobasic Salts.		*Ammonobasic Salts.*	
Basic mercuric fluoride	[illegible]		
Basic mercuric chlorides	$Hg_xO_yCl_z$	Basic mercuric chlorides	NH_2HgCl $NH_2HgCl,HgCl_2$ $(Hg_2NCl)_2.HgCl_2$
Basic mercuric bromide	$Hg_4O_3Br_2$	Basic mercuric bromides	NH_2HgBr $(Hg_2NBr)_4.HgBr_2$ $NH(HgBr)_2$ Hg_2NBr
Basic lead iodides	$xPbI_2.yPbO$	Basic lead iodide	$Pb_2NI.2NH_3$

Since it will be frequently necessary in the course of this article to speak of the acids, bases, and salts of this system and to describe a considerable number of reactions between these ammonia derivatives, it becomes desirable to formulate a scheme of nomenclature in order that the discussions which follow may be carried on as clearly and concisely as possible. A brief statement of the system of nomenclature which will be used is given herewith.

1. The author has already proposed (*Journ. Am. Chem. Soc.*, 1905, xxvii., 823) to designate the acids, bases, and salts of the ammonia or nitrogen system as *ammono acids*, *ammono bases*, and *ammono salts* respectively, which is to say that the acid amides and imides, including the amides and imides of the non-metallic elements, are ammono acids, the metallic amides and imides are ammono bases, and the metallic derivatives of the acid amides and imides are ammono salts (Note 4).

2. When it becomes desirable to distinguish between the acids, bases, and salts of the ammonia system, on the one hand, and those of the oxygen or water system on the other, it will be convenient to refer to the members of the latter system as *aquo acids*, *aquo bases*, and *aquo salts* (Note 5).

3. We shall find that compounds exist which are related to ammonia as the ordinary acid salts and basic salts—that is to say, the aquoacid salts and the aquobasic salts—are related to water. Such compounds will be called ammonoacid salts and ammonobasic salts respectively (Note 6), and the process whereby the ammonobasic salts are formed will be called *ammonolysis*. It will be shown that ammonolytic reactions take place in liquid ammonia solutions in a manner entirely analogous to the familiar hydrolytic reactions in water solutions.

4. We shall also have occasion to speak of compounds which are related to ammonia as the ordinary hydrated salts, or salts with water of crystallisation, are related to water. Obviously such compounds may very properly be called *ammonates*, just as salts with water of crystallisation are sometimes called hydrates, or they may be called either *ammonated salts* or *salts with ammonia of crystallisation*. (These designations have frequently been used by others).

5. Furthermore, when it becomes desirable to emphasise the distinction between a water-free salt and a salt with water of crystallisation or containing adsorbed water, the former is usually referred to as the anhydrous salt. Similarly, when it is desired to speak of ammonia-free salts, in contradistinction to a salt containing ammonia, either adsorbed or as ammonia of crystallisation, it will be convenient to speak of the former as *deammonated salts* or as *anammonous salts*. (A designation first used in print by Browne and Houlehan, *Science*, 1911, xxxiv., 284).

6. The relationship which the bases of the water system bear to the metallic oxides, on the one hand, and those which the acids bear to their anyhdrides on the other, are found to be exemplified by the relationship which exists between the acid amides and imides and the nitrides of the non-metallic elements or electronegative radicals, and between the metallic or basic amides and imides and the metallic nitrides. We shall therefore on occasion refer to the non-metallic nitrides as *acid nitrides*, or *acid anammonides*, and to the metallic nitrides as *basic nitrides*.

7. Finally, as there are amphoteric hydroxides and oxides, so we shall find it convenient to speak of those ammonia derivatives which show amphoteric properties as *amphoteric amides*, *imides*, and *nitrides*.

In the accompanying tables is given a selected list of compounds belonging to the water and ammonia systems respectively.

Notes.

4. Acetamide and diacetamide are accordingly ammonoacetic acids; the potassium derivatives of acetamide and sodium diacetamide are ammonoacetates of potassium and sodium respectively. Urea is ammonocarbonic acid and the potassium derivatives of urea obtained by Franklin and Stafford are potassium ammonocarbonates. Trinitroaniline is ammonopicric acid. Calcium cyanamide is the calcium salt of ammonocyanic acid.

5. The writer in another place (*loc. cit.*) has proposed the prefix hydro for the oxygen acids, bases, and salts, but submits that the word aquo, which he encountered in the writings of Werner ("Neuere Auschauungen auf dem Gebiete der anorganischen Chemie") is a much better designation. The generally accepted practice of referring to the aquo acids, bases, and salts as oxygen acids, bases, and salts would require us to designate the analogous derivatives of ammonia as nitrogen acids, bases, and salts, a procedure which is open to obvious objections.

6. Not basic ammono salts and acid ammono salts. The formulæ for three ammono basic salts are NH_2HgCl, NH_2HgNO_3, and $NH_2HgNH(CH_3CO)$; the first formula represents an ammonobasic halogen salt, the well-known infusible white precipitate; the second represents an ammonobasic aquo salt, a compound which has been recently prepared (Strömholm, *Zeit. Anorg. Chem.*, 1908, lvii., 72), and the third represents an ammonobasic ammono salt, a compound not known to exist but which may possibly be prepared by the action of potassium amide on acetamide mercury. An ammono salt may be expected to undergo either ammonolysis to form an ammonobasic ammono salt, such as represented by the last formula above, or hydrolysis to form an aquobasic ammono salt, such as represented by the formula $HCONHHgOH$, a compound which has been prepared by Fischer and Grützner (*Arch. Pharm.*, 1894, ccxxxii., 329).

(To be continued).

THE SCIENTIFIC WEEK.

(From Our Own Paris Correspondent).

THE PROTECTION OF NATURE'S FAUNA.

As president of the French delegation at the International Conference of Berne for the protection of nature's fauna, M. Edmond Perrier, director of the Natural History Museum, has communicated to the Academy of Sciences the principal decisions taken at the conference. M. Perrier recalls the fact that, unless a protective legislation be adopted by different countries, several species of animals will soon disappear. Thus, the large cetacea, such as the whale and cachalot, hunted excessively, especially by the Norwegian fishing societies, are doomed to rapid destruction. In ten years the rhinoceros and African elephants will also have disappeared unless the African hunting is put under control. The birds of paradise that are confined to New Guinea, a country not so large as England, and to the Solomon Islands, the extent of which is inferior to that of Corsica, are being veritably massacred. The aigrettes are undergoing the same fate. In presence of these facts, the conference under the presidency of M. Forter, a Swiss federal councillor, has decided to name a permanent international committee, which will hold its sittings at Bâle, and will meet at least once every three years. Each country adhering to the conference will be represented by at least two delegates. Each delegate will submit to their Government the proposals of the committee destined to bring about legislative measures in view of the efficacious protection of animals. Answering to a question of the secretary of the Academy, M. Darboux, M. Perrier added that the feather industry is trying to hinder all protective legislation. At the present time more than 50,000 workpeople are employed in plucking the skins of aigrettes, birds of paradise, and other birds. A feather worker earns about 4 francs a day to pluck 400 aigrettes. In face of the disappearance of aigrettes a feather merchant has appointed the Natural History Museum to award a prize of £400 to any one who succeeds in the breeding of these birds. But it is hardly probable that the prize can be awarded in the limits appointed by the giver. From all accounts it appears that the feather industry is very prosperous, while, on the other hand, there are at present 30,000 artificial flower makers in Paris without work. The feather has killed the flower.

MERCURY AND MUSTS.

The influence of mercury on alcoholic fermentation has just been studied by M. P. Nottin. The presence of mercury in a liquid in a state of fermentation produces two distinct phenomena. The mercury feebly attacked by the natural acid must produce toxic salts, which, according to their dose, keep back or hinder entirely the development of the yeast. Secondly, the mercury as a metal increases the production of the yeast, because it continually removes from the must its carbonic acid by a phenomenon of a purely physical order, and thus allows the yeast to breathe and vegetate more easily. Platinum and porous substances produce the same effect.

AUTUMN LEAVES.

The sumptuous gold and purple attire with which the autumn forests are bedecked has, for a very long time, puzzled numbers of learned men. Many physiologists have wondered what is the nature of this coloration. Prof. Gaston Bonnier has explained, before the Academy of Sciences the researches of M. Raoul Combes, who has been able to realise the production of the red substance of leaves outside the organism itself. Another scholar, M. Guilliermons, has studied the manner in which this red substance is produced from a histological point of view. The substance is produced by misochondries, those little living elements that are in the interior of all celulles. M. Raoul Combes has also shown that there exists in green leaves a yellowish substance, which he has isolated and crystallised, and it is this substance he has transformed into a red substance having identically the same point of fusion and the same properties as that which is extracted from reddened leaves. Now, it was supposed that this transformation took place under the influence of oxidation, but the proof was never given. M. Raoul Combes has shown that the contrary is the fact. It is by induction that the red substance is obtained at the expense of the yellowish substance of green leaves. It is easy to understand the importance of this question, for these researches are doubtless applicable to the coloration of all pink, violet, red, lilac, or blue flowers.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, November 27th, 1913.

Sir ARCHIBALD GEIKIE, K.C.B., President, in the Chair.

PAPERS were read as follows:—

"*Method of Measuring the Pressure produced in the Detonation of High Explosives or by the Impact of Bullets.*" By Prof. B. HOPKINSON, F.R.S.

A steel shaft about $1\frac{1}{2}$ inches diameter and 4 feet long is suspended horizontally from strings so that it can swing in a vertical plane as a ballistic pendulum. At one end it carries an end-piece of the same diameter and several inches long. The end-piece is held on by magnetic attraction; the surfaces of the joint are carefully faced. If a bullet be fired at the other end a wave of pressure travels along the shaft, whose length represents the duration of the blow on the scale 1 inch $= 5 \times 10^{-6}$ second approx. The wave passes the joint without change, and is reflected as a tension-wave from the free end. If length of wave exceeds twice that of end-piece, the tail of pressure-wave will have passed the joint when the head of tension-wave reaches it, and the piece will fly off, having trapped within it the whole momentum of the blow, leaving the shaft at rest.

By experimenting with different lengths of end-piece and finding that which is just long enough to stop the shaft, the duration of blow can be determined. The end-piece is caught in a ballistic pendulum and its momentum measured; thus, knowing the time, the average pressure is determined. By using shorter pieces and finding the percentage of total momentum trapped in each the maximum pressure exerted during blow can also be found.

Applied to investigation of the blow given by a lead bullet, the method gave results in close accord with those expected on the assumption that the bullet behaves as though it were liquid, the measured duration of blow being nearly that required by the bullet to travel its own length.

Measurements by the same method of pressures produced by detonation of a 1 oz. dry gun-cotton primer showed that, at a distance of $\frac{3}{4}$ inch from surface of cotton, the pressure is practically all gone in 1/50,000 second, the average pressure during that period being about 25 tons per square inch, and the maximum of the order of 45 tons per square inch. At surface of cotton the duration of blow is probably about the same and pressures roughly twice as great.

The bearing of these results on shattering of ductile steel plates by detonation of gun-cotton in contact with them is considered.

"*Gravitational Instability and the Nebular Hypothesis.*" By J. H. JEANS, F.R.S.

The work of Maclaurin, Jacobi, Poincaré, and Darwin, on rotating fluids has applied only to the abstract case in which the mass is considered perfectly incompressible and homogeneous. To estimate the bearing of their results on astronomical problems, it is important to know to what extent these results remain valid for actual compressible heterogeneous masses.

The result of the present investigation can be summed up very concisely by saying that the ideal mass of incompressible fluid has been found to supply a surprisingly good model by which to study the behaviour of the more com-

plicated natural systems considered in astronomy. The systems considered in the present paper are those in which the pressure p is a function of the density ρ, the special case in which the relation between p and ρ is given by Laplace's law $p=c(\rho^2-\sigma^2)$, and systems in which the matter, when free from rotation, is arranged in spherical layers, such that Laplace's law is obeyed in each layer, but the constants of the law vary from layer to layer. The problem especially under consideration has been that of determining the amount of rotation at which configuration of revolution (*e.g.*, spheroids) first become unstable. In so far as it has been found possible to examine this question, it has been found that, without exception, the compressible mass will behave up to this point in a manner almost exactly similar to the incompressible mass, and results, both qualitative and quantitative, obtained for the latter, will be true for the former. The compressible mass, set into rotation, will apparently pass through a series of stable flattened figures very similar to the Maclaurin spheroids. It will then for just about the same amount of rotation as the incompressible mass (rotation being measured by $\omega^2 \div$ [mean density]) leave the symmetrical form and assume a series of forms similar to the Jacobian ellipsoids. The main result appears to suggest that the work of Poincaré and Darwin is applicable to the bodies of nature and not merely to mathematical abstractions.

"*Diffraction of Light by Particles comparable with the Wave-length.*" By B. A. Keen, B.Sc., and A. W. Porter, F.R.S.

A suspension of finely-divided sulphur, obtained by precipitation from a solution of thiosulphate of soda by the addition of acid, ordinarily diffracts an excess of blue light, so that a white source of light seen through it looks red. One of us discovered that if the particles be allowed to grow the red image gradually changes over in colour, becoming at one stage a deep indigo blue, and afterwards passing through various shades of green to white.

The present investigation was undertaken to obtain quantitative information in regard to this phenomenon. Measurements of the intensity of the directly transmitted light were made for different colours by means of a Höfner spectrophotometer. The data obtained showed that for any particular colour the transmitted light diminishes up to a certain stage and then increases. The time in which the minimum intensity is reached is nearly proportional to the wave-length. Observations with a microscope showed that the size of particle for which the minimum occurs is from four to six times the wave-length. These are considerably larger than those examined theoretically by Lord Rayleigh. Some physico-chemical considerations are introduced in an attempt to connect the diameter with the time. The data are published with the object of attracting mathematicians to an interesting but difficult region of the subject of diffraction.

"*Colour of Zircons, and its Radio-active Origin.*" By Prof. R. J. Strutt, F.R.S.

"*Influence of the Constituents of the Crystal on the Form of the Spectrum in the X-Ray Spectrometer.*" By Prof. W. H. Bragg, F.R.S.

The energy of the pencil of X-rays which falls on the crystal of the X-ray spectrometer is in part spent within the crystal through absorption, which implies the production of cathode and characteristic X-rays, and in part is scattered, producing the reflected ray when circumstances are favourable. It is found that where there is much absorption there is little reflection.

It is known from Barkla's work that absorption coefficients show sharp discontinuities. Copper, for example, is relatively transparent to its own characteristic radiation, and to a lesser degree to the radiations of all substances of less atomic weight than its own. It is relatively opaque to the radiations of heavier atoms. Consequently, a copper screen placed across the path of the rays in the spectrometer reduces the intensities of the shorter waves far more than the intensities of the longer, the critical value being sharply defined. This is illustrated by an examination of the spectra of Os, Ir, Pt, Pd, Rh, Cu, and Ni, and of the effects of various screens.

The same effect is found to occur when the absorbing atom is within the crystal. Zinc blende gives a spectrum in which the A peak of Pt is very exceptionally strong in comparison with the rest of the spectrum, because zinc is relatively opaque to all shorter waves. Sodium arsenate gives a spectrum in which both the A and the B peaks are strong. There is no obvious resonance of any atom in the crystal to incident rays.

This implies that the scattering power does not show the same discontinuities as the absorption coefficients. There is, in fact, good evidence that the scattering power is proportional to the atomic weight. The reflecting power of a plane in the crystal depends on the sum of the weights of the atoms it contains and not on their nature. For instance, the alternate (100) planes of CaF_2 are equally effective, though they contain only Ca, and only F atoms alternately, because the atomic weight of Ca is nearly twice that of F.

The best reflectors are therefore those crystals of which the absorption coefficients are smallest in comparison with their weights or their scattering powers. For this reason alone the diamond must be a very good reflector.

"*Analysis of Crystals by the X-Ray Spectrometer.*" By W. L. Bragg.

The paper contains the results of the examination of various crystals by the X-ray spectrometer. The rays from bulbs with anti-cathodes of palladium or rhodium were used, as each of these metals gives off radiation consisting almost entirely of a single monochromatic component. By a quantitative comparison of the intensities of the successive orders of reflection by various crystal faces, it is shown that the X-ray spectrometer can be made to give a very complete analysis of the crystal structure. For instance, in the case of iron pyrites it is possible to find the relative positions of the interpenetrating lattices on which the iron and sulphur atoms are placed, to within 2 per cent of the distance between neighbouring points of the same lattice.

The structures particularly investigated [illegible]he paper are those of the isomorphous sulphides, py[illegible]es, and hauerite, and of the series of compounds which [illegible]pose the calcite family of minerals. By a study of the[illegible]st compounds, it is concluded that the diffracting power of an atom is proportional to its atomic weight.

"*Ship Resistance: The Wave-making Properties of certain Travelling Pressure Disturbances.*" By T. H. Havelock, D.Sc.

The paper contains a theoretical comparison of the wave-making resistance associated with certain distributions of surface pressure. Various inferences are drawn in regard to variation of resistance with speed, and the speeds at which typical interference effects occur. In particular, types are examined which are similar in general form to those associated with the motion of ship models in recent work at the William Froude tank in the National Physical Laboratory.

"*Mathematical Representation of a Light Pulse.*" By R. A. Houstoun, D.Sc.

The object of this paper is to call attention to a new series of expressions representing the initial form and dispersion of a light pulse. They have been suggested by one of Kelvin's hydrodynamical papers, and are derived from his instantaneous-plane-source solution in the conduction of heat.

For $t=0$ they give sharp symmetrical maxima descending to 0 within a short distance from the origin, and for t large they give well-defined groups of waves, in which the wave-length decreases from the front to the rear of the group.

The energy distribution of one of the groups obeys Wien's law for black-body radiation, and allows the height of the initial pulse in this case to be interpreted very simply in terms of the temperature.

CHEMICAL SOCIETY.

(Continued from p. 280).

244. "*Note on the Structure of certain Lactones formed by the Fission of the* gem.-*Dimethyl*cyclo*propane Ring.*" By William Henry Perkin, jun., and Jocelyn Field Thorpe. (*Trans.*, 1913, 1760).

The constitution of the lactone-dicarboxylic acids A and B described in a former paper (*Trans.*, 1901, lxxix., 764) and of lactone-dicarboxylic acids prepared by Baeyer (*Ber.*, 1896, xxix., 2792) and by Aschan (*Annalen*, 1913, ccxcviii., 299) is discussed.

245. "*The Resolution of* 2 : 3-*Diphenyl*-2 : 3-*dihydro* 1 : 3 : 4 *naphthaisotriazine into Optically Active Components.*" By William Jackson Pope and Clara Millicent Taylor. (*Trans.*, 1913, 1763).

The resolution of this base is effected by crystallisation with *d*-bromocamphor-π-sulphonic acid; the fractional crystallisation of the mixed salt which results yields two salts of the optically active acid, containing the *d*- and the *l*-base respectively. The liberation of the optically active base from the salts is accompanied by its complete optical inversion.

246. "*The Mutual Solubilities of Ethyl Acetate and Water and the Densities of Mixtures of Ethyl Acetate and Ethyl Alcohol.*" By Richard William Merriman. (*Trans.*, 1913, 1774).

The mutual solubilities of ethyl acetate and water have been determined by a method which enables a test of the accuracy of the results to be applied. Although contraction occurs in the formation of both of the saturated solutions, yet the solubility of ethyl acetate in water increases with rise of temperature, but the solubility of water in ethyl acetate decreases with rise of temperature. There is no point of maximum density of water saturated with ethyl acetate above 0°.

When alcohol is mixed with ethyl acetate a small expansion takes place; the maximum percentage expansion occurs when the two liquids are approximately in equimolecular proportions. A table of densities of mixtures of the two liquids is given.

247. "*The Azeotropic Mixtures of Ethyl Acetate, Ethyl Alcohol, and Water at Pressures above and below the Atmospheric Pressure.*" Part I. By Richard William Merriman. (*Trans.*, 1913, 1790).

The change in composition of the azeotropic mixture of ethyl acetate and water has been traced from 25 mm. to 1500 mm. pressure. The percentage of water increases continuously with the pressure, and there is no evidence of a constant value being reached at higher pressures. Assuming that the expression $p_1/p_2 = x/(1-x)$, where p_1 and p_2 are the partial pressures and x and $(1-x)$ are the molecular proportions of the two substances, holds for the azeotropic mixture, the partial pressure of the water has been calculated. At all temperatures this partial pressure is almost exactly equal to the vapour pressure of pure water at the same temperature. The Duhem-Regnault law, which states that in the case of partly miscible liquids the total pressure of the heterogeneous mixture is equal to the vapour pressure of the more volatile component in the pure condition, has been found to be erroneous.

248. "*The Azeotropic Mixtures of Ethyl Acetate, Ethyl Alcohol, and Water at Pressures above and below the Atmospheric Pressure.*" Part II. By Richard William Merriman. (*Trans.*, 1913, 1801).

The alterations in composition of the ester-alcohol binary mixture and the ternary mixture have been studied at pressures ranging from 25 mm. to 1500 mm. There is no evidence of constant composition being attained at any pressure.

Although the vapour-pressure curves of ethyl alcohol and ethyl acetate cross at a pressure of 948 mm., yet the percentage of alcohol in the azeotropic mixture increases continuously with the pressure, and shows no break at the point of crossing of the vapour-pressure curves. The following general rule for the change of composition of a binary azeotropic mixture of minimum boiling-point has been deduced from the present investigation:—The percentage of the liquid, for which dp/dt is the smaller, increases as the pressure decreases. The rule is followed in seven different cases. The only exception that has been found is the ethyl alcohol-water mixture (Wade and Merriman, *Trans.*, 1911, xcix., 997).

249. "*The Mechanism of the Condensation of Glucose with Acetone.*" By James Leslie Auld Macdonald.

Experience in the preparation of glucose-monoacetone and diacetone has shown that, however prolonged the treatment with acid acetone may be, glucose-monoacetone may always be isolated at the end of the reaction, and, moreover, the two condensation products are obtained in very variable yields. The conclusion is drawn that the formation of these compounds does not depend on the hydrolysis of glucose dimethylacetal, followed by condensation in definite stages with 2 molecules of acetone.

By arresting the condensation of glucose dimethylacetal with acetone at an early stage, *glucose dimethylacetal-εζ monoacetone* has been isolated as the main initial product. (The nomenclature adopted is that used in *Trans.*, 1913, ciii., 564). This compound is highly unstable towards heat and acids, and readily loses methyl alcohol, with the formation of *methylglucoside-εζ-monoacetone*. The position of the acetone residue in this compound was established by methylation by the silver oxide method, and subsequent hydrolysis of the product in two stages. In this way, *βγ-dimethyl methylglucoside-εζ-monoacetone*, *βγ dimethyl methylglucoside*, and lastly *βγ-dimethyl glucose* were obtained.

On the other hand, prolonged treatment of glucose dimethylacetalmonoacetone with acid acetone results in simultaneous hydrolysis and condensation taking place, and the formation of glucose diacetone. The di-derivative thus produced has therefore the acetone residues linked to the two pairs of carbon atoms, αβ and εζ respectively, a conclusion which harmonises with all the evidence available regarding the structure of this compound.

The condensation reactions of glucose dimethylacetal are thus extremely complex. When left in contact with acetone containing hydrogen chloride the initial products are glucose monoacetone and glucose dimethylacetalmonoacetone, the latter compound probably furnishing the chief source of glucose diacetone.

250. "*Condensation of Acid Chlorides with the Ethyl Esters of* (a) *Cyanocetic Acid*, (b) *Malonic Acid, and* (c) *Acetoacetic Acid.*" Part I. By Charles Weizmann, Henry Stephen, and Ganesh Sakharam Agashe. (*Trans.*, 1913, 1855).

A detailed description of work of which a preliminary account has already appeared (*Proc.*, 1912, xxviii., 103).

251. "2-*Phenyl*-5-*styryloxazole.*" By Robinson Percy Foulds and Robert Robinson. (*Trans.*, 1913, 1768).

In order to characterise 2-phenyl-5-styryloxazole the authors have prepared the substance by treating *styryl benzoylaminomethyl ketone* with concentrated sulphuric acid.

252. "*The Action of Sulphur Chloride and of Thionyl Chloride on Metallic Salts of Organic Acids: Preparation of Anhydrides.*" By William Smith Denham and Hilda Woodhouse. (*Trans.*, 1913, 1861).

The reaction between sulphur chloride and metallic salts of organic acids in the presence of an indifferent solvent, which is represented for the case of silver benzoate by the equation $2C_6H_5 \cdot CO_2Ag + S_2Cl_2 = (C_6H_5 \cdot CO_2)_2S_2 + 2AgCl$ (*Trans.*, 1909, xcv., 1237), has been found to be general for many types of acids. Salts of hydroxy- and amino-acids behave exceptionally. The compounds of the type $(R \cdot CO_2)_2S_2$ are in all cases unstable, and decompose spontaneously with separation of sulphur and formation o sulphur dioxide and the anhydride of the acid. Unde

similar conditions thionyl chloride usually yields sulphur dioxide, the acid anhydride, and the chloride of the metal (*Proc.*, 1909, xxv., 294), but in the case of hydroxy-acids intermediate compounds are formed, which, on loss of sulphur dioxide, give rise to anhydro-compounds. A crystalline *malic anhydride* has been prepared in this way.

The respective behaviours of sulphur chloride and thionyl chloride in these reactions are consistent with their possessing similar constitutions.

253. "*The Action of Magnesium Aryl Haloids on Glyoxal.*" By Henry Wren and Charles James Still. (*Trans.*, 1913, 1770).

*iso*Hydrobenzoin, *αβ-dihydroxy-αβ-di*-p-*tolylethane* (m. p. 161·8—162·6°), and *αβ-dihydroxy-αβ-di-o-tolylethane* (m. p. 116·5—118°) have been prepared by the action of magnesium phenyl bromide, magnesium *p*-tolyl bromide, and magnesium *o*-tolyl bromide respectively, on unimolecular glyoxal (Harries and Temme, *Ber.*, 1907, xl., 165). In no case could definite evidence of the formation of the second theoretically possible isomeride be obtained. The *acetyl* derivatives corresponding with the two latter glycols melt at 105—106° after softening at 103—104°, and 99—100° after softening at 98·5° respectively.

254. "*The Miscibility of Solids. Part II. The Influence of Chemical Constitution on the Thermal Properties of Binary Mixtures.*" By Ernest Vanstone. (*Trans.*, 1913, 1826).

The method of thermal analysis has been applied to binary mixtures of the type PhαβPh.

Pascal and Norman (*Bull. Soc. Chim.*, 1913, [4], xiii., 151, 201) have shown that dibenzyl, stilbene, tolane, azobenzene, and hydrazobenzene are miscible in all proportions in the solid state; also that with benzylaniline, benzylideneaniline, and phenyl benzyl ether eutectic diagrams are obtained, and solid-solution formation is limited.

A series of thermal diagrams for benzoin and benzil with these substances has been determined. In each case the diagram shows a single eutectic point and limited formation of solid solutions.

The eutectic point depends on the melting-points of the constituents. It is always found nearer the substance of lower melting-point. The molecular volumes at the temperatures of their melting-points of ten substances have been determined. Substances containing oxygen have the greatest molecular volumes.

The exceptional behaviour of benzil, when compared with other symmetrical compounds of the type PhααPh, is discussed, and the greater molecular domain of benzil is suggested as the cause of its lower degree of miscibility.

255. *The Solubilities of Alkali Haloids in Methyl, Ethyl, Propyl, and isoAmyl Alcohols.*" By William Ernest Stephen Turner and Crellyn Colgrave Bissett.

The solubilities, in methyl, ethyl, propyl, and *iso*amyl alcohols, of lithium chloride and iodide, sodium chloride and iodide, potassium chloride, bromide, and iodide, and rubidium chloride have been determined. Measurements were made at a common temperature of 25°, and in the case of lithium chloride in ethyl alcohol, also over the range from 0° to 60°.

The existence of the compound $LiCl,4C_2H_6O$, first indicated by Simon, was confirmed, and its transition-point into lithium chloride fixed at 17·4°. A compound $LiI,4C_3H_8O$, stable at 25°, was also found, and another, $NaI,3CH_4O$, stable at 15—16°.

The solubilities at 25° proved that solvent action, on the above salts, decreases continuously in passing from water through the series of alcohols; that the order of solubility is iodide>bromide>chloride, and that, in all the solvents, the solubility of the alkali chlorides is in the order:—Lithium chloride>sodium chloride>rubidium chloride>potassium chloride.

256. "*Nitration of 1-Chloro-2 : 4-dinitronaphthalene.*" By Max Rindl.

A solution of 1-chloro-2 : 4-dinitronaphthalene in cold concentrated nitric acid deposits on keeping prismatic crystals of *1-chloro-2 : 4 : 5-trinitronaphthalene*, melting at 143—144°. After several weeks *1-chloro-2 : 4 : 8-trinitronaphthalene* begins to be deposited, along with the 1-chloro-2 : 4 : 5-trinitronaphthalene. The chlorine atom in both of these compounds is mobile. By treatment with aqueous solutions of alkali hydroxides they are converted into the corresponding trinitronaphthols. Only the 2 : 4 : 5-trinitro-α-naphthol can be reconverted into the corresponding chlorotrinitronaphthalene by means of *p*-toluenesulphonyl chloride and diethylaniline. Other reactions depending on the mobility of the chlorine atom are the formation of 2 : 4 : *5-trinitro-α-naphthyl methyl ether* and of amines, for example, 2 : 4 : *5-trinitro-α-naphthylamine*, as well as mono- and di-substituted alkyl and aryl amines. Copper powder removes the chlorine, and two molecules join together, forming dinaphthyl derivatives. In the case of 1-chloro-2 : 4 : 5-trinitronaphthalene a secondary reaction takes place, resulting in the elimination of chlorine and its replacement by hydrogen, with the formation of 1 : 3 : 8-trinitronaphthalene.

257. "*The Decomposition of Carbamide.*" By George Joseph Burrows and Charles Edward Fawsitt.

Previous investigations on the decomposition of carbamide in aqueous solutions by one of the authors (*Zeit. Phys. Chem.*, 1902, xli., 603) have been extended to solutions in aqueous alcohol.

Addition of alcohol decreases the velocity of decomposition, but does not alter the mechanism of the reaction, which is a unimolecular one.

The theory already put forward that carbamide is not hydrolysed by water or aqueous solutions of acids is confirmed.

Carbamide decomposes primarily into ammonium cyanate, and is then decomposed into carbonate.

The authors believe that the decomposition of carbamide is the first chemical reaction to be investigated (1902), the mechanism of which demands the assumption of intermediate products, the existence of which has been proved.

258. "*The Viscosity of Sugar Solutions.*" By Charles Wilfred Roberts Powell.

The results of an investigation into the viscosities of aqueous solutions of sucrose, dextrose, and lævulose are given, dealing first with simple solutions containing only one of the sugars, and then with complex solutions containing mixtures of them.

The effect of temperature on the viscosity of these solutions is found to be well expressed by Poiseuille's equation—

$$\eta_t = \frac{\eta_0}{1 + \alpha t + \beta t^2},$$

where η_0 is the viscosity at 0°, η_t is the viscosity at $t°$, and α and β are constants. If the concentration of the solution is expressed as grms. of solute per grms. of solvent, the relation between viscosity and concentration is a logarithmic one, and may be represented by the equation $\eta_x = A^x$, where x is the concentration and A a constant.

A new method of calculation of the viscosity of simple solutions is discussed, the time of flow of each of the constituents of the solution being calculated. By this means it is thought possible to examine the change in viscosity of the solute in concentrating solutions, as distinct from the change in viscosity of the solution.

A possible explanation of the deviation of the increase in viscosity of solutions with increasing concentration from any simple law is outlined. The theory given does not attempt to explain fully the question of viscosity, but indicates how the friction between different groups of molecules in the solution may definitely characterise the order of the change in viscosity with change in the composition of the solution.

It was found that for aqueous solutions of the three sugars mentioned, the two equations—

$$\eta x = A x ,$$

$$\eta = \frac{m\eta a + n\eta b}{(m + n)}$$

may be used conjointly with a fair degree of accuracy to calculate the viscosity of a solution containing two or more of the sugars.

259. "*The Rate of Hydration of Acid Anhydrides: Acetic, Propionic, Butyric, and Benzoic.*" By Bernard Howell Wilsdon and Nevil Vincent Sidgwick.

The velocity of this change was measured by Rivett and Sidgwick's method (*Trans.*. 1910, xcvii., 732) by observing the rise in conductivity of the solution.

The conductivity of acetic acid was measured at 18°, of propionic at 18° and 25°, and of butyric at 25°. Approximately constant values of the dissociation constant are obtained in dilute solution if the conductivity of the water used is added to that of the solution.

The rate of hydration of the corresponding anhydrides was measured at the same temperatures, and also that of benzoic anhydride at 25°. The velocity of change of acetic anhydride is about twice that of propionic, about four times that of butyric, and about eight times that of benzoic.

With acetic anhydride at 18°, as was previously observed by Rivett and Sidgwick at 25°, the velocity decreases steadily with increase of concentration above about 0·2N; the same occurs with propionic anhydride above about 0·02N. The correction for the diminution in the concentration of the water only accounts for a small part of this fall. If, however, the activities of the two reacting molecules (water and anhydride) are assumed to be proportional to the fluidity of the solution, and the observed velocities are multiplied by the square of the viscosity, the results are found to be constant (for both anhydrides and at both temperatures) within the limits of experimental error.

Monochloroacetic anhydride was found to be hydrated with a velocity too great for measurement—at least one hundred and fifty times that of acetic anhydride.

260. "*Investigations on the Dependence of Rotatory Power on Chemical Constitution. Part IV. The Rotatory Powers of the Secondary Alcohols of the Formula* $C_2H_5 \cdot CH(OH) \cdot R$." By Robert Howson Pickard and Joseph Kenyon.

A description is given of the synthesis and resolution of thirteen alcohols of the series $C_2H_5 \cdot CH(OH) \cdot R$. These optically active carbinols have been examined polarimetrically in the homogeneous state, and in alcoholic and in benzene solution. The results show that, whilst the molecular rotatory powers gradually increase as the series is ascended, there are further exaltations when the growing chain contains about five and about ten carbon atoms. It has been shown also that a similar effect on the molecular rotatory powers of the series $CH_3 \cdot CH(OH) \cdot R$ is only noticeable when these are determined in solution, as in the homogeneous state the molecular rotatory powers of the carbinols of this series increase regularly with the mass of the compounds.

The optical rotatory dispersive power of the higher members of the series is a constant, and is independent of the temperature (from 20° to 160°).

PHYSICAL SOCIETY.

Ordinary Meeting, November 14th, 1913.

Prof. C. H. Lees, Vice-President, in the Chair.

A paper entitled "*On the Thermal Conductivity of Mercury by the Impressed Velocity Method,*" by H. Redmayne Nettleton, B.Sc., was read by Dr. A. Griffiths.

The paper gave an account of the determination of the thermal conductivity of mercury at the ordinary temperature of the room by the impressed velocity method first described by the author in the *Proceedings* of this Society, vol. xxii., 1910. The mercury is contained within a vacuum-jacketed syphon tube about 17 sq. cm. in cross-section, which is heated at the top and maintained ice-cold at its lower extremity. The distribution of temperature down this tube is determined with the aid of a single thermo-junction, while the mercury is at the same time flowing uniformly up the tube at speeds ranging from 870 to 1420 grms. per fifteen minutes. The calorimetry is thus essentially continuous flow calorimetry within the temperature gradient, the quantity of heat passing down the mercury being controlled and measured by the flow of liquid. The wires forming the thermo-elements—viz., iron and constantan—were contained within a vertical tube of 6 mm. external diameter, through the glass of which the wires were fused; this carrier tube lay within the vacuum vessel. The thermo-junction could be raised or lowered to the desired extent by a cathetometer, or could be rotated in a horizontal plane. The isothermals were found to be remarkably horizontal.

If θ_1 is the temperature at a distance $L/2$ above the isothermal surface at a temperature equal to that of the enclosure, and θ_2 the temperature at an equal distance below, then $\log_e \theta_1 / \theta_2 = msL/2KA$, where s is the specific heat of mercury, K its thermal conductivity, A the cross-section of the tube, and m the mass of mercury crossing a section per second. Using this relationship a mean value of 0·0201 c.g.s. units at 15·5° C. is obtained for K.

The advantages of the method lie in the simplicity of the calorimetry and in the fact that temperature ratios rather than temperature differences are required.

Discussion.

Dr. C. Chree said there might be some doubt as to the exactitude with which the mathematical formulæ represented the physical facts, but the method seemed promising for determining the change with temperature of the thermal conductivity, and he inquired whether investigations had been directed towards that end. As the cross-section of the vessel appeared in the formulæ, it would give increased confidence if vessels of different section were tried and found to give accordant results.

Dr. J. A. Harker asked if the author was satisfied as to the distribution of the flow at different parts of the cross-section, and wished to know how the results compared with those of other observers.

Mr. F. E. Smith said that it appeared to him that the practice of Mr. Nettleton did not exactly tally with the conditions imposed by theory. Why did Mr. Nettleton assume that the temperature of some water in a glass tube in the proximity of the apparatus was the same as that of the outer wall of the vacuum jacket? It appeared from the data that it was not, and this being so an error was introduced, inasmuch as the isothermal taken as the "zero isothermal" was not so. If the assumed "zero isothermal" was appreciably higher than the true one the deduced thermal conductivity would be too high. Again, theory imposed a condition on the outer wall of the vacuum jacket; it must be of uniform temperature. Was this so in practice? One end of the jacket was practically at 0° C, and the other at 100° C.; there must be a temperature gradient. He would suggest that the outer wall of the vacuum jacket be cooled with circulating water in which the second thermo-junction was immersed. The beauty of Mr. Nettleton's method was apparent to all, and he trusted he would continue his experiments.

Dr. A. Russell regretted that the author, following the usual custom, called the law for the cooling of a body by radiation Newton's law, and the coefficient the Newtonian coefficient of emissivity. Newton considered the case of a block of iron being cooled by a current of air, so that the heat lost by radiation was very small compared with that lost by convection. In this case he found that the heat lost by the iron was very approximately proportional to the difference of temperature between the air and the iron. This law had been verified recently up to differences of

temperature between the cooling body and the air as high as 200° C. and 300° C. In the author's experiment, however, the tube had a vacuum jacket, so that the heat lost by convection was quite negligible. As the difference of temperature was, comparatively speaking, small, we saw by Stefan's law that the author's assumption was justifiable. In the speaker's opinion the real "Newton's law of cooling" was of great importance in practical work, and he thought that teachers and the writers of text-books ought to lay greater stress on it.

Dr. W. H. Eccles called attention to the fact that at first sight the method would be thought to be incapable of high accuracy, because of the form of the expression for K, the conductivity. This expression had as its denominator what was practically the difference between two nearly equal magnitudes, and these magnitudes were themselves differences. That was to say, the denominator was of the nature of a second differential coefficient of an experimental curve. That such consistent results were obtained indicated remarkable precision of experiment.

Prof. Lees asked how small a difference of temperature throughout the cross-section would have been detected by the thermo-couple.

Dr. Griffiths, in reply, stated that, as shown in the earlier paper, the distribution of the flow was not important, so long as the isothermals were plane.

The Author communicated the following:—In reply to the Chairman, Prof. Lees, it should be stated that a difference of temperature of 0·05° C. over a horizontal surface would easily have been detected in any position of the cathetometer. In the neighbourhood of the "zero isothermal" all resistances, except that of the galvanometer and wires, could be removed and a more delicate test made. It is safe to say that in this neighbourhood a difference of 0·02° C. would have been detected easily. Thus the isothermals are remarkably horizontal, the result far exceeding the author's expectations. Mr. F. E. Smith has raised an important point in his remarks about the "cold junction" at the temperature of the enclosure. The cold junction could not be inside the vacuum, as iron and constantan cannot be fused through glass and a vacuum of high standard maintained. An attempt to surround an earlier vacuum vessel with a glass water jacket (it is necessary to be able to see through the vacuum when adjusting the carrier-tube) resulted in its collapse, and no risks were taken with the present vessel, which is valuable, as at least ten attempts at making a third have failed. The "cold junction" was maintained in a tube under water just outside the vacuum vessel to protect it from air draughts, but on holding it in the air just outside the vacuum vessel no serious temperature difference was recorded. The vacuum, of course, was of "thermos" or X-ray standard. When the "warm junction" was in such a position as to produce no electric current the zero-isothermal was located. The author cannot doubt that the temperature of the cold junction was rightly that of the enclosure: for it stood the double test of Newton's law holding with respect to it in a statical experiment, as well as the constancy of the ratio $\log \frac{\theta_2}{-\theta_2}/L$ in many dynamical experiments. The height of the zero-isothermal varies in every experiment, being higher the faster the flow, as can be seen in the actual temperature curves given in the paper previously alluded to. Under no flow the zero was very low, being near the lower extremity of the vacuum-jacketed portion of the experimental tuba—too low, in fact, to allow of the test $\theta_1/-\theta_2=1$ over any considerable range.

A paper entitled "*Polarisation and Energy Losses in Dielectrics*" was read by Dr. A. W. Ashton, M.I.E.E.

The object of the paper is to discuss the relations which should exist between the coefficients in Pellat's equation (as modified by Schweidler), giving the displacement in a viscous dielectric as a function of the time of charge and the P.D.

Taking the modified equation—

$$D_t = KE_0 + KE_0\Sigma\epsilon(1-e^{-at})$$

the charging current for constant voltage becomes for $t>0$ $i_t = KE_0\Sigma a\epsilon e^{-at}$, and in the series of exponential terms a and ϵ can be so chosen as to make $\Sigma a\epsilon e^{-at} = \beta t^{-n}$.

The author makes the following deductions among others:—Where the polarisation current is proportional to t_{-n}, the viscous capacity of any group of molecules having the same time constant of displacement is proportional to the $(1-n)$th power of the time constant.

For values of n between 0·5 and 1·5 the maximum energy loss occurs in those groups for which a does not greatly differ from p, where $p=2\pi n$.

For all positive values of n less than 2, the alternating current conductivity is proportional to the nth power of the frequency.

Experiments by Addenbrooke, Fleming and Dyke, Curtis and H. A. Wilson are quoted in support of the theoretical deductions. The paper includes a brief *résumé* of Pellat's theory.

Discussion.

Dr. Russell said that the author's method was ingenious, and that the formula deduced for the dielectric current agreed well with many experimental results. He thought, however, that Pellat's theory was not sound and that von Schweidler's modification of it was too elaborate to be of much practical use. He pointed out that Dr. Grover had proved that, from the mathematical point of view, Hopkinson's and von Schweidler's theories were identical. He considered that Fleming and Dyke's experimental results could not be ignored, and that none of the theories advanced up to the present explained them satisfactorily. Very different formulæ gave results which were practically identical over wide ranges, and so they were of doubtful help in enabling us to discover the causes of the phenomena. He considered that the nomenclature of dielectric theory stood badly in need of standardising. For instance, what the author called the displacement was practically the same as Maxwell's electric displacement, but Sir J. J. Thomson and several other writers called it the polarisation.

Dr. Eccles stated that the paper compelled remark on the artificial nature of Pellat's hypothesis. This hypothesis led to an expression for the displacement current as a sum of exponential terms. Experiment required it to be a power of t, or the sum of several power terms. This required that the exponential terms of Pellat's hypothesis should be infinite in number—which deprived the hypothesis of physical meaning. It would be more logical, therefore, to begin with the power terms as fundamental, and to discard the false start given by Pellat.

Mr. Addenbrooke stated that in order to get at the proper theory of experiments the best dielectrics should not be used, as the effects were so minute that the chances of error were great. With poorer dielectrics, the actions were on a greater scale and easier to observe. Using an ellipsoid suspended at 45° to the electric field, he had been able to carry his experiments down to a frequency of one cycle in two hours, taking, of course, time readings of current and voltage. Dr. Ashton had not mentioned a paper by Wagner, which seemed to cover much the same ground.

Prof. C. H. Lees mentioned a later paper on the subject by Curtis, who had found that Schweidler's equations held if several terms were taken.

Dr. Ashton, in reply, said that in Pellat's original paper there were results which showed that over a certain range the charging current could be represented by a constant times t^{-n}, and that more than one exponential term might be required. His own experiments showed that $i_t = \beta t^{-n}$ held over two or three days. The difficulty was to keep the temperature constant over a long time. Another difficulty was that if circuit were broken for a fraction of a second, the results were vitiated. In reply to Dr. Russell, he believed $i_t = \beta t^{-n}$ represented Fleming and Dyke's results better than $i_t' = a + bt$.

A paper entitled "*A Lecture Experiment to Illustrate Ionisation by Collision and to show Thermo-luminescence*" was read by Mr. F. J. HARLOW.

A method of demonstrating to an audience both ionisation by collision and the reduction of the sparking potential by the presence of initial ionisation is described in the paper.

A spherical bulb, in which an electrodeless discharge is excited, contains two coils of platinum wire, coated with lime and aluminium phosphate respectively, which can be heated by means of a current. Within the range of pressure for which the electrodeless discharge can be excited, provided the discharge is not too intense, both the lime and aluminium phosphate, on being raised to incandescence, give a considerably increased effect, showing that the ions given off by these substances are effective under the action of the induced E.M.F. in producing an enormous number of others by collision.

The lower limit of the range of pressure over which the discharge can be excited with a given induced E.M.F. is considerably extended by heating either the lime or the aluminium phosphate, the former, however, being much more efficient than the latter in this respect. This extension of range is an illustration of the fact that the sparking potential is diminished by the presence of ions, and by negative ions more than by positive.

If the lime and aluminium phosphate are subjected while cold to an intense discharge for some time they exhibit the phenomenon of thermo-luminescence, the lime on being warmed gently giving out a golden yellow luminosity and the aluminium phosphate a blue. The effect with lime apparently increases with an increase of electrical activity caused by continued heating, which suggests that the thermo-luminescence and electrical activity are closely associated. This suggestion receives support from the fact that lime alone does not exhibit thermo-luminescence, and that both lime on platinum and lime on nickel, which are electrically active, do. Further experiments are being made on this point, which the author thinks will throw light on the origin of the anomalous electrical activity of lime on platinum.

A demonstration of these experiments was given.

INTERNATIONAL ASSOCIATION OF CHEMICAL SOCIETIES.

EXTRACT FROM THE MINUTES OF THE THIRD SESSION OF THE COUNCIL.

AT the third session of the Council of the International Association of Chemical Societies, held at the Institut Solvay, Parc Léopold, Brussels, from September 19 to 23, 1913, Prof. Haller gave an account of the negotiations which had taken place between M. Ernest Solvay and certain representatives of the International Association, and which had resulted in the offer by M. Solvay of an unconditional gift of 250,000 francs to the Association. M. Solvay further proposed to found an "International Institute of Chemistry," having for its object the facilitation of the study and progress of chemistry, without, however, excluding problems belonging to other branches of the natural sciences, provided that these have some bearing on the science of chemistry. The Institute will be governed by an "Administrative Commission" of three Belgian members (one nominated by His Majesty the King of the Belgians, a second by the University of Brussels, and a third by M. Ernest Solvay), and by a Delegation of the Council of the International Association of Chemical Societies, consisting of Messrs. Haller, Ostwald, and Ramsay. Of the Institute's annual income of from 55,000 to 56,000 francs two-thirds will be placed at the disposal of the International Association of Chemical Societies, whilst the remaining one-third will be employed in establishing scholarships for Belgian students. The Council gratefully accepted M. Solvay's offers, and further passed the following resolution:—"Ces sessions se tiendront autant que possible une fois sur deux à Bruxelles." M. Solvay has provided the International Association with offices in Brussels, where the archives will be kept, and a permanent secretary is to be appointed to take charge of them and to conduct the general business of the Association.

Prof. Haller was elected President of the Association for the ensuing year, and it was decided that the next meetings should be held in Paris some time during the first fifteen days of September, 1914.

Prof. Guye presented a report on the "Unification of Abbreviations of Titles for Scientific Journals used in Chemical Memoirs," and it was decided that, should the editors of all journals publishing chemical memoirs consider it advisable, the Council of the International Catalogue of Scientific Literature should be consulted, and a list of abbreviations should be circulated among the societies affiliated to the Association, with an invitation definitely to adopt the abbreviations for all future publications.

Prof. Werner read and explained the Report of the Commission appointed to consider the question of "the mitigation of the difficulties arising from the existing multiplicity of languages employed in scientific literature," and after prolonged discussion the Committee was reappointed to report to the next meeting of the Council, more particularly on three points:—

(*a*) The publication of an International Journal of Abstracts in three languages.

(*b*) The publication of three editions of an International Journal of Abstracts, namely, in English, French, and German.

(*c*) The publication of an International Journal containing translations into either English, French, or German of original papers appearing in the lesser known languages.

The Council received and adopted the report from the Commission for the Unification of Physico-Chemical Symbols. The following list gives some of the symbols recommended:—

Angström unit (10^{-10} metre)	Å
Density	d
Gas constant per mole	R
Mean free path	λ/
Micron (10^{-6} metre)	μ
Millimicron (10^{-9} metre)	$\mu\mu$
Number of molecules	N
Pressure	p
Osmotic pressure	P
Van der Waal's constants	a, b
Volume (in general)	v
Volume, specific	v_s
Volume, atomic	v_a
Volume, molecular	v_m
Atomic weight and grm. atomic weight	A
Concentration (units not specified)	c
Equilibrium constant	K
Mole fraction	x
Molecular and grm. molecular weight	M
van 't Hoff coefficient	i
Velocity coefficient	k

The Committee received the report from the Inorganic Nomenclature Committee, and adopted the recommendations contained therein. The following symbols are adopted:—

I for iodine,
Xe for xenon,
W for wolfram,
Nb for niobium,

and Be is strongly recommended for beryllium. The Committee recommends that in indexing inorganic compounds the constituent atoms, including carbon, should be arranged in alphabetic order, making exceptions, however,

for hydrogen and oxygen, which should always be placed at the end of the formula. The recommendations of the Austrian and Russian National Committees for indicating the relative number of atoms of each element in the molecule are approved; *e.g.*, N_2O_5 becomes dinitrogen pentoxide instead of nitrogen pentoxide. In order to obtain shorter names for substances it is considered desirable to indicate the valency of the positive component by means of a suffix, the valencies one to eight being represented by the suffixes *o*; *a*, *i*, *e*, *on*, *an*, *in*, *en* in the order given; *e.g.*, the two chlorides of mercury would be respectively named mercuro- and mercura-chloride. It is recommended that an International Commission, composed of one member from each country represented in the Association, be appointed with Prof. Werner as chairman.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances des l'Académie des Sciences. Vol. clvii., No. 17, October 27, 1913.

Refraction and Magnetic Rotation of Compounds with Acetylenic Function.—Ch. Moureu, P. Th. Muller, and J. Varin.—The proximity of the triple bond and of a negative (or slightly saturated radical) gives rise in the fatty series to a more or less marked exaltation of the refraction, which is greatly increased in the aromatic series by the proximity of the triple bond and the phenyl group. The rotation is qualitatively affected in the same way as the refraction (except in the case of acetylenic diacetal, which exhibits a depression). But if a table showing the relative exaltations is consulted, it is seen that the magnetic rotation is more sensitive than the refraction to the reciprocal influence of the slightly saturated radicals and the acetylenic bond. This sensitiveness is specially noticeable in the aromatic series.

Preparation of Aluminium Ethylate.—Clément Berger.—Aluminium ethylate can be prepared by the action of aluminium amalgam on absolute alcohol containing a little sodium ethylate. A small amount of sodium is dissolved in alcohol, and sheets of aluminium, amalgamated by immersion in a saturated solution of mercuric chloride, are introduced into the solution. Bubbles of hydrogen are produced, and a grey precipitate of aluminium ethylate containing a little alumina is deposited. $3C_2H_6O + Al = (C_2H_5O)_3Al + 3H$. Aluminium ethylate is very readily decomposed by water, and hence all traces of moisture must be avoided. It is decomposed by heat.

Presence of Gallium in Commercial Aluminium and its Separation.—Ch. Boulanger and J. Bardet.—Gallium appears to be very widely distributed in nature, and the spectrographic examination of many specimens of commercial aluminium always revealed its presence very distinctly. To separate it the aluminium was dissolved in HCl, and the metal always present, such as Cu, As, Sb, Sn, Pb, Zn, Fe, Na, is separated by appropriate treatment; *i.e.*, by sulphuretted hydrogen in either hydrochloric or acetic solution. After this treatment had been repeated three times only the gallium and a small amount of iron remained. Finally, treatment with boiling potash completely eliminated the iron.

Metallic Phosphides derived from P_5H_2.—R. Bossuet and L. Hackspill.—By the action of liquid ammonia the alkaline phosphides, P_5M_2, are converted into crystalline ammoniacal phosphides, which are soluble in liquid ammonia. In this state they undergo double decompositions with metallic salts dissolved in the same solvent. From these reactions precipitates of phosphides are obtained of varying colour according to the metal contained in them; their general formula is P_5M, analogous to that of lead phosphide, P_5Pb, which has been analysed. All these compounds may be regarded as salts of the acid P_5H_2, which is Le Verrier's solid hydrogen phosphide.

Hydrogenation of Secondary Alcohol derived from Furfurol.—Roger Douris.—The hydrogenation of ethylfurfurylcarbinol over reduced nickel gives a mobile liquid from which the following products can be separated by fractional distillation:—(i.) Boiling-point 127—130°, under atmospheric pressure. The products are chiefly propyloxybutane and propyloxybutadiene. (ii.) Boiling-point 140—150°, under atmospheric pressure. This fraction contains dipropylketone. (iii.) Boiling-point 87—90°, under 15 mm. pressure. The principal product is ethyltetrahydrofurfurylcarbinol. (iv.) Boiling-point 110—120°, under 15 mm. pressure. This fraction is a very syrupy liquid in which there is a glycol, $C_8H_{16}O_2$.

Action of Magnesium Methyl and Ethyl Iodides on Michler's Ketone.—P. Lemoult.—When magnesium methyl iodide acts on Michler's ketone the hydrocarbon $CH_2 = C(Dm)_2$ is obtained. If the liquid, which is left after all this hydrocarbon is deposited is examined, it is found to contain three compounds:—(i.) The dimer of $CH_2 = C(Dm)_2$. (ii.) A compound containing 83 per cent C, 8 per cent H, 9 per cent N. (iii.) A compound containing 82 per cent C, 8 per cent H, 10 per cent N. With the ethyl compound the only product is the hydrocarbon $CH_3—CH = C(Dm)_2$.

MISCELLANEOUS.

Simple Process to Detect Nitrous Acid in presence of Nitric Acid.—A. Leclère.—An equal volume of a syrupy solution of citric acid is added to the solution to be analysed. Thus a dense liquid is obtained, and by means of a drawn-out pipette a 3 or 4 per cent solution of ammoniacal ferrous sulphate can be superposed on it. In presence of nitrous acid a brown ring appears at the surface of separation of the two liquids; while even a concentrated solution of a nitrate gives no reaction, since citric acid does not expel nitric acid from its salts. In presence of sulphides it is best to treat the solution with zinc acetate and filter off the zinc sulphide formed.

MEETINGS FOR THE WEEK.

MONDAY, 15th.—Royal Society of Arts, 8. (Cantor Lecture). "The Measurement of Stresses in Materials and Structures," by Prof. E. G. Coker, D.Sc.

TUESDAY, 16th.—Physical, at 3 and 7. Exhibition of Physical Apparatus. "Soap Films, by L. Brennan. "Production of Vibrations on Loaded and Unloaded Strings," by J. A. Fleming.

WEDNESDAY, 17th.—Royal Society of Arts, 8. "The Channel Tunnel," by Arthur Fell, M.P.

— Microscopical, 8. "The Binocular Microscopes of the Past, and a New Form of the Instrument," by C. Bock.

THURSDAY, 18th.—Chemical, 8.30. "Chemical Examination of Sarsaparilla Root," by F. B. Power and A. H. Salway. "Aromatic Compounds obtained from the Hydroaromatic Series—Part III., Bromoxylenols from Dimethyldihydroresorcin," by A. W. Crossley and N. Renouf. "Equilibrium of Dilute Hydrochloric Acid and Gelatin," by H. R. Procter. "Metallic Derivatives of Acetylacetone and Acetyl-mesityl Oxide," by G. T. Morgan and H. W. Moss. "Constitution of the Ortho-diazoimines — Part IV., Isomeric Benzenesulphonyl-3:4-tolylenediazoimides" by G. T. Morgan and G. E. Scharff. "Organic Derivatives of Silicon—Part XXI., The Condensation Products of Diphenylsilicanediol," by R. Robison and F. S. Kipping. "Sorption of Gases by Celluloid," by V. Lefebure,

THE CHEMICAL NEWS.

Vol. CVIII., No. 2821.

THE ANALYSIS OF ILKLEY SPA WATER.

By B. A. BURRELL, F.I.C.

Modern Ilkley occupies the site of the Brigantian stronghold of Llecan, which subsequently became the Roman station of Olicana.

"Ichley Fountaine" has been in repute for bathing for about two centuries, a small bath-house having been built in 1699 ("White's Directory of the West Riding of Yorkshire," 1838, vol. ii., p. 511). Hearne's edition of Leland's Itinerary contains a letter written by Dr. Richardson in 1709 stating :—"Ilkley . . . chiefly famous for a cold well, which has done very remarkable cures in scrofulous cases by bathing, and in drinking of it."

In 1734 Dr. Short wrote :—"Ichley Spaw springs out of the middle of a Mountain, a Mile high. . . . The Water is very clear, brisk, and sparkling; has no taste, colour, nor smell different from the common Water, is of the same weight. Its Basin and Course are of no other Dye than that of a common spring. . . . Five pints of this Liquor exhaled left 7 Grains of sediment. . . . Therefore, tho' this Water is of the greatest Esteem and Repute of any in the North of England, in the King's Evil and other old Ulcers; yet it derives these effects neither from its fixt nor volatile Parts, but wholly from the Coldness and Purity of the Element."—("The Natural, Experimental, and Medicinal History of the Mineral Waters of Derbyshire, Lincolnshire, and Yorkshire," by Thomas Short, M.D., of Sheffield; London, 1734, p. 307).

Dr. Rutty, in 1757, quotes from another treatise of Short's, specifying the virtues of the "Ichley Water."—("A Methodical Synopsis of Mineral Waters," by John Rutty, M.D.; London, 1757, p. 23).

Dr. Adam Hunter's examination in 1819 gave :—Temp. of water, 48° F.; temp. in shade, 64° F.; sp. gr. at 55° F., 1·00015.

A wine gallon was found to contain :—

	Grains.
Muriate of lime	6·50
Muriate of magnesia	3·00
Total	9·50

Gaseous contents—

	Cubic inches.
Carbonic acid gas	12·60
Atmospheric air	5·40
	18·00

Quantity 100 gallons per minute, and situate nearly three-quarters of a mile from the village ("An Essay on Two Mineral Springs at Harrogate, and on the Springs at Thorp-Arch and Ilkley," by Adam Hunter, M.D.; Leeds, 1819).

T. Shaw, M.R.C.S., in 1830, states ("The History of Wharfedale") :—"The water is, perhaps, for its purity, tenuity, and coldness, the best qualified . . . of any water in this part of the country. It has been frequently analysed, but the decomposition always proved that it contains no medicinal quality, . . . it is purity and softness only, which makes it more efficacious . . . than any other water known."

There is a reference to the water in the "Spas of England—Northern Spas," vol. i., by A. B. Granville, M.D., F.R.S.; London, 1841). The author having repeatedly measured the flow, which he puts at 60 gallons a minute, the temperature being 47° F., and that of the atmosphere 55° F. The analysis of Dr. Hunter is quoted.

William West, in 1844, states that he had not analysed it, but gives its composition in grains per gallon (*Brit. Assoc. Notices*, 1845, p. 107).

Chloride of sodium	0·657
Sulphate of soda	0·366
Sulphate of lime	0·2
Carbonate of lime	2·353
Carbonate of magnesia	1·04
Silicate of soda	1·066
Peroxide of iron	0·060
Total..	5·742

The following analysis is given in some of the local guides. The author is not stated.

	Grains per gal.
Sulphate of sodium	2·939
Chloride of calcium	0·572
Carbonate of calcium	2·185
Silica	1·200
Chloride of sodium	0·501
Solid matter	10·796
Free carbonic acid	6·581 cubic inches per gal.

Temperature, 43—45° F.

For several years past the writer has taken samples of the water from the pipe used for filling the Roman bath at the White Wells, the height of which is about 660 feet above sea-level. The water issues from the middle or third grits of the millstone grit series. Variations in temperature are very slight. The following readings selected from those made on ten different occasions show the extreme variations :—

Temperature of air (shade).	Temperature of water.
16·9° C.	8·8° C.
9·4° C.	7·7° C.

The water is clear and free from sediment. The general procedure was that recommended by Fresenius, and all numbers given are the mean of at least two, and generally of three or four determinations. For substances present in minute quantity the residues obtained by the evaporation of from 45 to 50 litres of the water were used. With such quantities neither bromine, iodine, barium, or strontium could be detected. International Atomic Weights, 1912, were used for the calculations.

The constituents are as follow—

	Grms. per litre.		Grains per gal.
SiO_2	0·0152	=	1·0641
SO_4	0·0176	=	1·2368
N_2O_5	0·0001	=	0·0093
Nitrous acid	None	=	None
P_2O_5	Trace	=	Trace
Cl	0·0110	=	0·7700
Fe	0·00016	=	0·0112
Al	Trace	=	Trace
Ca	0·0169	=	1·1866
Mg	0·0090	=	0·6307
Na	0·0119	=	0·8331
K	0·00125	=	0·0876
Li	0·00019	=	0·0136
Free ammonia.. ..		=	0·0011
Albuminoid ammonia		=	0·0020
Oxygen absorbed in 4 hours at 26·6° C.			0·0016

Taking into account the composition of the filtered boiled water, the acids and bases may be combined as follows, the numbers being in grains per gallon :—

Ferric oxide, Fe_2O_3	0·0159 (a)
Calcium carbonate, $CaCO_3$	0·8078
Calcium nitrate, $Ca2NO_3$	0·0140
Calcium silicate, $CaOSiO_2$	2·0535
Calcium sulphate, $CaSO_4$	0·5199
Magnesium carbonate, $MgCO_3$ ..	1·4235
Magnesium sulphate, $MgSO_4$ ..	1·0900
Potassium carbonate, K_2CO_3 ..	0·1548
Sodium carbonate, Na_2CO_3	0·8726
Sodium chloride, NaCl	1·1550
Lithium chloride, LiCl	0·0831
	8·1901

Total solid constituents dried at 173° C., 8·295.

(a) Ferrous carbonate, 0·0232.

The analyses of the gases and the results of the bacteriological examination will form the subject of a further paper.

THE AMMONIA SYSTEM OF ACIDS, BASES, AND SALTS.*

By EDWARD C. FRANKLIN.

(Continued from p. 285).

6. *Ammono Acids.*—The acid amides and imides derived from organic acids constitute a group of well known compounds, since practically every known carboxylic and sulphonic acid furnishes such a derivative. The amides and imides of the inorganic acids are not so well known, although in recent years several such compounds have been prepared and studied, among others especially the amides of sulphuric (Note 7) and nitric acids (Note 8) and the amides and imides of the acids of phosphorus (Stokes, *Am. Chem. Journ.*, pp. 1893—1898).

The members of the large group of acid amides and imides, in so far as they are soluble, give solutions in liquid ammonia which discharge the colour of alkaline solutions of phenolphthalein (Note 9), conduct the electric current, dissolve certain metals, and react with metallic amides, in a manner described in detail below, to give representatives of the class of ammono salts. The strength of these ammono acids, if it be assumed that their strength is indicated by the conductivity of their solutions in liquid ammonia and by the extent to which their salts resist the hydrolytic action of water, varies through quite as wide limits as do the ordinary oxygen acids. Acetamide and carbamide, at one extreme, for example, form solutions in liquid ammonia, which have scarcely more than an appreciable conductivity, and their potassium salts are completely hydrolysed in the presence of water. Toward the other extreme may be mentioned such ammono acids as phthalimide, nitrobenzenesulphonamide, nitrourethane, nitroguanidine, saccharin, &c., which dissolve in ammonia to form good conducting solutions (Franklin and Kraus, *Journ. Am. Chem. Soc.*, 1905, xxvii., 191), and which form salts of the alkali metals which are more or less stable in the presence of water.

Further compounds which are to be included among the ammono acids are the amides and imides of the non-metallic elements. Just as the halogen derivatives of the strongly electronegative elements, such as arsenic, phosphorous, boron, silicon, are completely hydrolysed by the action of water, so we may expect the same compounds to undergo decomposition in contact with liquid ammonia, with the formation of products bearing relations to this solvent analogous to those which the hydrolytic products bear to water.

The following equations, giving the results of recent work, show that in fact such ammonolytic reactions take place:—

$3TeCl_4 + 16NH_3 = Te_3N_4 + 12NH_4Cl$ (Metzner, *Comptes Rendus*, 1897, cxxiv., 32).

$B_2S_3 + 6NH_3 = B_2(NH)_3 + 3NH_4SH$ (Stock and Blix, *Ber.*, 1901, xxxiv., 3039).

$BCl_3 + 6NH_3 = B(NH_2)_3 + 3NH_4Cl$ (Joannis, *Comptes Rendus*, 1903, cxxxv., 1106).

$PCl_3 + 5NH_3 = P(NH)NH_2 + 3NH_4Cl$ (Joannis, *Ibid.*, 1904, cxxxix., 364).

$AsCl_3 + 6NH_3 = As(NH_2)_3 + 3NH_4Cl$ (Hugot, *Ibid.*, 1904, cxxxix., 54).

$SiCl_4 + 8NH_3 = Si(NH_2)_4 + 4NH_4Cl$ (Lengfeld, *Am. Chem. Journ.*, 1899, xxi., 531; Vigouroux and Hugot, *Comptes Rendus*, 1903, cxxxvi., 1670).

$SiS_2 + 4NH_3 = Si(NH)_2 + 2NH_4SH$ (Blix and Wirbelauer, *Ber.*, 1903, xxxvi., 4220).

$SiSBr_2 + 4NH_3 = SiS(NH_2)_2 + 4NH_4Br$ (Blix, *Ber.*, 1903, xxxvi., 4219).

Tellurium nitride, Te_3N_4, is an acid nitride or an acid anammonide; boron imide, $B_2(NH)_3$, and boron amide, $B(NH_2)_3$, are ammonoboric acids; phosphorus imide amide, $NH=P \cdot NH_2$, is an ammonophosphorous acid; arsenious amide, $As(NH_2)_3$, is an ammonoarsenious acid; silicon amide, $Si(NH_2)_4$, and silicon imide, $Si(NH)_2$, are ammonosilicic acids, and sulphosilicourea, $SiS(NH_2)_2$, is a sulphoammonosilicic acid. As is pointed out below, at least some of these ammono acids may be expected to react with potassium amide to give the corresponding potassium ammono salts.

Representatives of still another class of ammono acids are the nitroanilines which are related to ammonia as the nitrophenols are related to water. Just as the acid properties and electrical conductivities of aqueous solutions of the nitrophenols increase rapidly with the number of nitro groups present in the benzene ring, so in the case of the nitroanilines it has been found that while ammonia solutions of aniline are practically non-conductors, dinitroaniline gives a solution which is a good conductor, and trinitroaniline forms solutions which approach the salts in the facility with which they convey the electric current (*Journ. Am. Chem. Soc.*, 1905, xxvii., 197). Metallic derivatives of trinitroaniline have not been prepared, although Franklin and Stafford have shown the probable existence of a potassium salt (*Am. Chem. Journ.*, 1902, xxviii., 102).

It is interesting in this connection to note other and similarly marked strengthening of the acid properties of certain acid amides by the introduction of negative groups. For example, liquid ammonia solutions of acetamide, urea, and urethane are very poor conductors, while cyanoacetamide, nitroguanidine, and especially nitrourethane (Franklin and Kraus, *Journ. Am. Chem. Soc.*, 1905, xxvii., 205), form solutions which are excellent conductors. As was pointed out above, some of these ammono acids form salts which are stable in aqueous solutions, and in consequence have been prepared in considerable number in the past.

7. *Ammono Bases.*—The metallic amides, imides, and nitrides constitute a group of substances by no means so numerously represented among known compounds as is the case with the ammono acids. And among those that are known, as with the aquo bases it is the hydroxides of the alkali metals only which are soluble to any extent in water, so it is the amides of the alkali metals which are soluble in ammonia. Indeed, among the ammono bases potassium amide only (probably also rubidium and cæsium amides) is abundantly soluble.

Potassium amide has long been known, having been first prepared by Gay-Lussac and Thénard ("Recherches Physico-chimiques," 1811, i., 337) by heating metallic potassium in contact with gaseous ammonia. It is most conveniently prepared by the action of liquid ammonia on the metal in the presence of platinum black. The reaction between the metal and ammonia, which otherwise takes place very slowly (Joannis, *Comptes Rendus*, 1891, cxii., 502), is so greatly accelerated by the presence of the catalyser that any quantity of the amide may thus be very

* From *American Chemical Journal*, xlvii., No. 4.

easily made (Franklin, *Jour. Am. Chem. Soc.*, 1905, xxvii., 831). Potassium amide crystallises from cold concentrated liquid ammonia solutions in the form of beautiful colourless leaflets. Its solutions in liquid ammonia are good conductors of electricity (Franklin, *Zeit. Phys. Chem.*, 1909, lxix., 290; Arrhenius's "Zubelband"). The basic properties of potassium amide are shown by its behaviour toward liquid ammonia solutions of phenolphthalein, and by its action on liquid ammonia solutions of oxygen acids, halogen acids, and ammono acids, and also by its action on metallic zinc. Its behaviour toward oxygen acids and halogen acids is represented by the equations $KNH_2 + NH_4NO_3 = KNO_3 + 2NH_3$, $KNH_2 + NH_4Cl = KCl + 2NH_3$. The action of potassium amide on the ammono acids and on metallic zinc is discussed in some detail further on in this paper.

Taking advantage of the solubility of potassium amide, the writer has been able to prepare a number of insoluble metallic derivatives of ammonia by bringing soluble metallic salts and potassium amide together in liquid ammonia solutions (*Journ. Am. Chem. Soc.*, 1905, xxvii., 833). The new substances are thus obtained as precipitates which may be purified and analysed and their identity thereby established. It has been found that potassium amide in ammonia solution reacts with silver nitrate to form silver amide, with lead nitrate or iodide to form lead imide, with mercuric bromide and iodide to form mercuric nitride, and with bismuth bromide and iodide to form bismuth nitride. These reactions are represented by the following equations:—

$AgNO_3 + KNH_2 = AgNH_2 + KNO_3$,
$Pb(NO_3)_2 + 2KNH_2 = PbNH + 2KNO_3 + NH_3$,
$3HgI_2 + 6KNH_2 = Hg_3N_2 + 6KI + 4NH_3$,
$BiBr_3 + 3KNH_2 = BiN + 3KBr + 2NH_3$.

The close analogy between these reactions carried on in liquid ammonia solutions and the corresponding reactions in the water system will be clear from a comparison of the above equations with the following:—

$2AgNO_3 + 2KOH = Ag_2O + 2KNO_3 + H_2O$,
$Pb(NO_3)_2 + 2KOH = PbO.xH_2O + 2KNO_3 + (1-x)H_2O$.
$HgCl_2 + 2KOH = HgO + 2KCl + H_2O$,
$2BiCl_3 + 6KOH = Bi_2O_3.xH_2O + 6KCl + (3-x)H_2O$.

Just as in water solutions it is sometimes the hydroxide and at other times the oxide which is obtained, so in the case of the action of potassium amide on a silver salt in liquid ammonia it happens to be the amide which is formed; lead salts under similar treatment happen to give the imide, a deammonation product of the amide; while mercury and bismuth salts give neither the amide nor imide but in their stead the final deammonation product, the nitride.

In addition to the four ammono bases prepared as described above, Fitzgerald (*Journ. Am. Chem. Soc.*, 1907, xxix., 656) has shown that potassium amide acts upon cupric nitrate in solution in liquid ammonia to form cuprous nitride in accordance with the equation $3Cu(NO_3)_2 + 6KNH_2 = Cu_3N + 6KNO_3 + N + 4NH_3$; and it has been recently shown in this laboratory that a nitride of thallium is formed after the manner represented by the equation (experimental results not yet published) $3TlNO_3 + 3KNH_2 = Tl_3N + 3KNO_3 + 2NH_3$.

The new ammono bases thus obtained are insoluble in liquid ammonia, but dissolve readily in ammonia solutions of appropriate ammonium salts. Four of them—silver amide, lead imide, cuprous nitride, and thallium nitride—are amphoteric in character, for in addition to being soluble in ammonium salts, that is, in acids, they are also soluble in solutions of potassium amide. When dry, they all explode with more or less violence when heated or subjected to shock. Silver amide especially is so sensitive that it was only by exercising the greatest care that the isolation and analysis of the substance were accomplished. With the exception of mercuric nitride they are completely hydrolysed by the action of water with the evolution of ammonia and the formation of aquo bases. This exceptional behaviour of mercuric nitride is significant, as will be discussed in detail in a subsequent paper.

Soluble salts of a number of other metals, including calcium, barium, aluminium, ferrous and ferric iron, cadmium, magnesium, platinum, and nickel, have been found to give precipitates when treated in liquid ammonia solutions with potassium amide. It therefore appears certain that by this method a very considerable number of new metallic amides, imides, and nitrides may be prepared.

Before leaving the subject of the ammono bases it may be worth while to state that attempts have been made to prepare amides of the formulæ $(CH_3)_4N{\cdot}NH_2$, $(CH_3)_3S{\cdot}NH_2$, and $(C_6H_5)_2I.NH_2$ by the action of potassium amide on tetramethylammonium chloride, trimethylsulphonium iodide, and diphenyliodonium iodide respectively, but as yet without success.

Other ammono bases which have been prepared and are found described in the literature are the amides of zinc, sodium, lithium, rubidium, cæsium, calcium, barium, and strontium, the imide of lithium, and a considerable number of metallic nitrides.

8. *Ammono Salts.*—The obvious parallelism between water and its derivatives, the acids, bases, and salts on the one hand, and ammonia with its family of derivatives, the metallic amides, the acid amides, and the ammono salts on the other, led the writer, collaborating with O. F. Stafford, to study in some detail the reactions between the acid and basic amides in solution in liquid ammonia (*Am. Chem. Journ.*, 1902, xxviii., 83). The result of these studies was to show that the acid amides, which discharge the red colour of an alkaline solution of phenolphthalein in liquid ammonia, react with soluble metallic amides, which give the characteristic red colour with the same indicator, to form metallic derivatives of the acid amides in a manner strictly analogous to the familiar formation of salts in aqueous solution by the interaction of the ordinary acids and bases. For example, acetamide and potassium amide react with each other in ammonia solutions to form monopotassium acetamide, a compound which must be called an ammonoacid salt—acid for the reason that it contains a hydrogen atom replaceable by metal—and dipotassium acetamide, a normal salt, in accordance with the equations—

$$CH_3CONH_2 + KNH_2 = CH_3CONHK + NH_3$$

and—

$$CH_3CONH_2 + 2KNH_2 = CH_3CONK_2 + 2NH_3,$$

which are seen to represent reactions which are analogous to the familiar action of acetic acid on potassium hydroxide in aqueous solution. In addition to these two compounds, Franklin and Stafford prepared the sodium salt of acetamide and the potassium salts of a considerable number of other acid amides (*loc. cit.*), among them urea and sulphamide, the ammonia analogues of carbonic and sulphuric acids respectively. Formulæ for some of these salts are given in the tables (*ante*). In general, any ammonia derivative containing a negative element or radical may be expected to react with any derivative of ammonia containing a positive element or radical to give a salt-like compound as represented by the equations $MNH_2 + AcNH_2 = MNHAc + NH_3$, $2MNH_2 + AcNH_2 = M_2NAc + 2NH_3$, &c.

Stafford and Franklin have also shown that ammono salts may be prepared by the reaction of ammonia solutions of ammono acids on certain metals. For example, acetamide in solution in liquid ammonia reacts upon metallic sodium in accordance with the equations—

$$CH_3CONH_2 + Na = CH_3CONHNa + H,$$
$$CH_3CONHNa + Na = CH_3CONNa_2 + H,$$

and upon metallic magnesium in a manner represented by the equation—

$$2CH_3CONH_2 + 4NH_3 + Mg = (CH_3COH)_2Mg.4NH_3 + 2NH,$$

which, as will be readily recognised, are equations which are strictly analogous to those representing the action

acetic acid on metallic sodium and magnesium respectively.

Magnesium benzenesulphonamide, $(C_6H_5SO_2NH)_2Mg$, and magnesium cyanoamide, CNNMg, were similarly prepared by the action of liquid ammonia solutions of the acid amides upon the metal.

Some of the ammono salts prepared by Franklin and Stafford are readily soluble in liquid ammonia, others are but slightly soluble or insoluble. Certain of them separate from solution with ammonia of crystallisation. They are hydrolysed completely in the presence of water. Their solutions in liquid ammonia are probably good conductors of electricity, although, unfortunately, this has been proved experimentally for but one representative of the class. Liquid ammonia solutions of mercuric succinimide are excellent conductors (*Journ. Am. Chem. Soc.*, 1905, xxvii., 196).

The soluble members of the class of ammono salts should also enter into metathetic reactions in liquid ammonia solutions, giving precipitates of insoluble ammono salts when the necessary metallic ion is added to their solutions. A solution of potassium acetamide, when added to a solution of silver iodide, for example, may be expected to give a precipitate of an ammonoacetate of silver. Unfortunately, however, such reactions have not yet been studied quantitatively.

A considerable number of metallic derivatives of the acid amides, that is to say, compounds belonging to the class of ammono salts, have been prepared in the past and are found described in the literature. It will be sufficient for our purpose to call attention to a few representative compounds.

Gal (*Bull. Soc. Chim.*, 1883, xxxix., 647) has prepared the zinc salts of acetamide, butyramide, benzamide, carbamide, and oxamide by the action of zinc amide, an ammono base, on the respective acid amides in ethereal solution, and Titherley (*Journ. Chem. Soc.*, 1897, lxxi., 461) has obtained the sodium derivatives of formamide, acetamide, propionamide, and benzamide by the continued action of hot benzene solutions of the acid amides on sodium amide (*Journ. Chem. Soc.*, 1897, lxxi., 461). The reactions whereby these products have been obtained are identical with those studied by Franklin and Stafford, excepting that the former were carried on in solvents other than liquid ammonia. Gal's and Titherley's compounds, like those prepared by Franklin and Stafford, are completely hydrolysed in the presence of water.

Salts of the stronger ammono acids, that is to say, the metallic derivatives of acid amides containing stronger electronegative groups, are capable of resisting the hydrolytic action of water to a greater or less extent, which accounts for the fact that a considerable number of such compounds—as, for example, the potassium and sodium salts of succinimide, phthalimide, saccharin, the nitrobenzenesulphonamides, and the nitroamines (Franchimont, *Rec. trav. chim.*, 1894, xiii., 308), nitrourea, nitrourethane, nitroguanidine (Thiele and Lachmann, *Liebig's Ann. Chim.*, 1895, cclxxxviii., 267), benzenesulphonnitroamide, &c. (Hinsberg, *Ber.*, 1892, xxv., 1093), have been prepared in the past from aqueous and alcoholic solutions.

The mercury and silver salts of the acid amides show a much greater resistance to the hydrolysing action of water than do the ammono salts of other metals. Mercuric ammono salts especially are unique in this respect. Mercuric acetamide, for example, is so very stable in the presence of water that even aqueous potassium hydroxide fails to effect its hydrolysis.

The metallic derivatives of the acid amides and imides have just been discussed at some length as members of the large class of ammono salts. The fact has not been forgotten, however, that the acid amides of oxygen acids are tautomeric substances (Hantzsch, *Ber.*, 1901, xxxiv., 3142); that is to say, they are compounds which behave sometimes in accordance with the one, and at other times in accordance with the other, of the two formulæ, $R—CONH_2$ and $R—C{:}NHOH$. The first formula represents the acid amide as an ammono acid, the second as a mixed aquo ammono acid. It may therefore well be that certain metallic derivatives of the acid amides, for example, acetamide mercury, are true ammono salts, whereas others, as potassium acetamide, are aquo salts. Certainly, however, in such a compound as dipotassium acetamide, one of the potassium atoms must be in combination with the nitrogen, and is therefore to that extent, at least, an ammono salt. Similarly, the metallic salts of other of the acid amides and imides mentioned above may be the tautomers of the true ammono salts. Potassium succinimide, for example, may be given the formula $\begin{array}{l} CH_2CO \\ | \\ CH_2—C—OK \end{array}\!\!>\!N$ instead of $\begin{array}{l} CH_2CO \\ | \\ CH_2CO \end{array}\!\!>\!NK$; and potassium methylnitroamine, the formula $CH_3—N{:}NOOK$ instead of $CH_3—NK—NO_2$.

However all this may be, no such possibilities exist in connection with the metallic derivatives of the oxygen-free amides. In such compounds as silver cyanoamide, CNNHAg, potassium methylcyanoamide, $CNN(CH_3)K$, potassium succinimidine, $\begin{array}{l} CH_2—C(NH) \\ | \\ CH_2—C(NH) \end{array}\!\!>\!NK$, &c., there can of course be no question of the manner in which the metal is combined.

A considerable number of compounds belonging to the class of ammono salts are probably to be prepared by the action of potassium amide or of metallic potassium upon the non-metallic amides and imides, and perhaps even by the action of potassium amide upon the non-metallic nitrides. The only compound of this kind yet obtained is a potassium ammonotitanate, of the formula $N{\equiv}Ti—NHK$, which has been prepared in the chemical laboratory at Stanford University by Mr. T. B. Hine by the action of potassium amide in excess on titanium bromide (experimental results not yet published). The reaction is repre- by the equation—

$$TiBr_4 + 5KNH_2 = N{\equiv}Ti—NHK + 4KBr + 3NH_3.$$

Notes.

7. Traube, *Ber.*, 1892, xxv., 2472; 1893, xxvi., 610; Hantzsch and Holl, *Ibid.*, 1901, xxxiv., 3435; Ruff, *Ibid.*, 1903, xxxvi., 2900; Franklin and Stafford, *Am. Chem. Journ.*, 1902, xxviii., 95; Franklin and Kraus, *Journ. Am. Chem. Soc.*, 1905, xxvii., 191; Franklin, *Zeit. Phys. Chem.*, 1909, lxix., 300.

8. Thiele and Lachmann, *Liebig's Ann. Chem.*, 1895, cclxxxviii., 267; Franklin and Kraus, *Journ. Am. Chem. Soc.*, 1905, xxvii., 191.

9. A large excess of such an acid as acetamide is required to discharge the red colour of a solution of phenolphthalein which has been rendered alkaline by potassium amide, obviously for the reason that acetamide is a very weak acid whose salts in solution in liquid ammonia are highly ammonolysed.

(To be continued).

Carbon Nitrides.—H. Pauly and Ernst Waltzinger.—When the tetraiodide of imidazol is heated it gives up three atoms of iodine at 180°, and the fourth at 420°, the final product being the substance C_3N_2. C_3N_2 like paracyanogen gives dicyanogen at 800—900°, $C_3N_2 = (CN)_2 + C$. The product obtained at 180° is C_3N_2I, and resembles amorphous carbon. When α- or μ-methyl tri-iodo-imidazol and tetraiodopyrrol are heated the products are $C_3N_2.CH_3$ and C_4NH respectively. They both give cyanogen when heated. When heated with soda lime they give up all their nitrogen as ammonia, and they readily dissolve in fused alkalis; ammonia is slowly given off, and CO_2 and HCN appear in the melt. These compounds seem to belong to a new class of substances, to which paracyanogen also belongs.—*Berichte*, xlvi., No. 13.

THE SCIENTIFIC WEEK.

(From Our Own Paris Correspondent).

The Light of the Marine Abysses.

The depths of the oceans and seas have for a long time excited the curiosity of learned men. An unknown fauna has been revealed by the soundings effected during the cruisings of the Prince of Monaco. One question, however, remained obscure: that of the penetration or light into the marine abysses. Was it complete obscurity or slight luminescence? M. Klaus Grein has just made known in the *Annales of the Oceanograph Institute* the result of the researches he undertook for the last two years in the transparent waters of the island of Capri. The absorption of light by sea-water is progressive. From a depth of 5 metres the bluish violet rays form more than the half of the totality of light. M. Grein and his collaborator, M. Ewald, have then searched, with the help of sensitive films in the bluish violet region of the spectrum, what is the quantity of light that penetrates into the depth of the water. He took as a luminous unity the quantity of light existing at a depth of 3 metres. At 20 metres the light decreases by half, by two-thirds at a depth of 30 metres, and five-tenths at 40 metres from the surface. At a depth of 75 metres only a fiftieth part of the light existing at 3 metres depth passes, and only the three hundred and thirtieth part at a 100 metres from the level of the sea. Other experiments have been made at Monaco by this physicist. He has remarked that at a depth of 50 metres only a two-millionth part is to be found of the red light existing at 1 metre; orange resists longer. But it is in the green part of the spectrum that the luminous intensity is the slowest to diminish. The blue-green and the blue-violet penetrate even to the deepest depths. At 1000 metres there are ten times more blue-violet than blue-green; at 1300 metres and more these rays still make an impression on the plate. The light as it penetrates further and further through water diminishes in intensity. It descends beneath the threshold of human vision, beneath that of the assimilation of plants, but it is never extinguished.

The Erosion of the Sea Coasts.

In the war that the sea is daily waging against the coasts the land is often vanquished. The sea often, indeed, advances far inland, but there are also certain points where it is known to recede before the new land that emerges from the waves. The modifications of the southern coast of Brittany between Peumarch and the river Loire have just been studied from this point of view by M. La Porte, hydrographic engineer of the navy, who has compared the surveys of 1820 executed by Messrs. Beautemps and Beauchamp with the quite recent surveys effected from 1901 to 1911 by the hydrographic ordnance service. The conclusion of M. La Porte's paper, which has been presented before the Academy of Sciences by M. Hatt, is that the coast is receding towards the west of an axis passing by Quiberon, and is rising in the east. In the Morbihan district, on the contrary, a remarkable stability of the coast-line is to be observed. The maximum displacement seems to be about 12 centimetres in a century. Thus, in a region situated to the west of Quiberon the sea has taken on an average about 40 metres from the coast, and in some places as much as 60 metres in a hundred years. Towards the Loire, on the contrary, it is the land that is enroachiug on the sea.

Radio-culture.

M. Stoklasa, of Prague, is continuing his researches on radio-culture. He has been able, by submitting different cultures to radio-active action, either natural or artificial, to considerably increase the weights of the crops, compared with those produced by ordinary culture, it is essentially useful to rigorously dose the radio-active energy put into play, for same influence, after a certain maximum is reached, becomes unfavourable, and may even bring about the death of the plant. These results, communicated by Prof. Maquenne, are of the greatest interest from a biological and also from an agronomical point of view, for it is quite possible that big agricultural enterprises may, in the long run, benefit by these early indications. As a matter of fact, it suffices, in order to put into practice M. Stocklasa's experiments, to water the ground with water naturally radio-active, which may sometimes be procured without difficulty, or else water charged with emanations of radium may be employed. It may, perhaps, be that in the activity of the soil or the sub-soil is to be found an explanation of the particular fertility of certain regions, which up till now has not been thoroughly understood, either by the composition of the soil or by the climatic conditions of the spot.

SIR JOHN CASS TECHNICAL INSTITUTE.

The Annual Prize Distribution was held on December 10th, when the prizes were distributed by Sir Thomas H. Elliott, K.C.B., Deputy Master and Comptroller of the Royal Mint. The Chair was taken by Sir Owen Roberts, M.A., D.C.L., Chairman of the Governing Body of the Institute.

Sir Thomas Elliott, in addressing the students, spoke of the desirability of keeping in view the aim of the instruction provided at the Institute, the object of its work, and the extent to which this object was being accomplished. He was himself disposed to say that the primary purpose for which the Institute exists is to assist students to do justice to themselves and to those who may be or become dependent upon them, to enable them to perform services which the community requires and for which the community is prepared to pay and to pay well, to increase their earning powers, and so to help them to secure a better livelihood for themselves than would otherwise be theirs. At the same time he, of course, fully realised that men could not live by bread alone, but that the building up of the bodily health, the broadening of the mental powers, and the development of the moral character were also essential to individual happiness and national prosperity. The achievement of these things is, however, much more difficult unless a man has continuous, regular, and remunerative employment, and it is to assist in making sure of such employment that the work of the Institute is mainly directed. Sir Thomas Elliott also counselled the students not to be afraid of selecting a manual occupation, and in connection with it to endeavour to learn all the facts connected with the material used, the machinery employed, and the scientific principles upon which the work is based. With such knowledge, students should be in a position to take advantage of the two or three chances which come to most men in the course of their lifetime of rising out of the rank and file and of getting as it were their commission with all its attendant privileges and responsibilites. In this connection also he advised the students to be a little adventurous and ambitious and not to play overmuch for safety.

The Rev. J. F. Marr, M.A., Chairman of the Institute Committee, gave a summary account of the work of the Institute during the past session, in which he referred especially to the increasing number of students, the research work that had been carried on in the Institute both by students and by members of the staff, and the several developments in the courses of instruction provided; in this latter connection details were given of the work on Colloids, on the Theory and Applications of Mathematical Statistics, on the Fermentation Industries, on Mine Sampling and Valuing, on Metals used in the Motor Car Industry, and on the Casting of Metals, all subjects which had received the special attention of the Governing Body during the past session.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, December 4th, 1913.

Sir William Crookes, O.M., President, in the Chair.

Papers were read as follows:—

"*On a Method of Studying Transpiration.*" By Sir Francis Darwin, F.R.S.

In order to study the effect of external conditions on the evaporation of water from leaves, it is necessary to exclude the action of the stomata from the problem, because the opening and closing of these apertures practically increase and diminish the evaporating surface. This is evident, since the leaf is made up of transplanting cells and intercellular air spaces, and it is the connection of these spaces with the outer air that is controlled by the stomata.

The method I employ is to close the stomata by coating the surface of the leaf with vaseline or some other grease, and then to place the intercellular spaces in connection with the outer air by cutting the leaf into strips. It is found by experience that such leaves transpire at rates comparable to those observed in natural leaves, and that they appear to behave normally in relation to external influences. In the present paper the effect of the relative humidity of the air is considered.

The diagrams constructed from the experiments show in a general way the obvious fact that transpiration falls off as the air becomes more charged with moisture. The diagrams also illustrate the well-known fact that transpiration continues in saturated air in consequence of the temperature of the leaf being above that of the air. This is well known to be due to the respiration of the leaf, and is of interest that the diagrams give a means of calculating of leaf temperature.

Finally, my results point to an improved but rough method of expressing the relation between transpiration and the psychometric condition of the air. This makes it possible, in studying the effect of other conditions on transpiration, *e.g.*, the action of light, to introduce a correction for psychrometric differences.

"*The Effect of Light on the Transpiration of Leaves.*" By Sir Francis Darwin, F.R.S.

The method employed is that described in my paper "On a Method of Studying Transpiration." The stomata are closed by a coating of vaseline, and the intercellular spaces are placed in communication with the outer air by means of slits or other incisions in the leaf. In this way we avoid the difficulty inherent in the problem of normal transpiration, viz., that this process is regulated by apertures (the stomata) which are constantly varying in size.

The object of the research was to get a general idea of the differences in transpiration produced by alternate periods of diffused light and darkness. The experiments were made on the laurel (*Prunus laurocerasus*) and the ivy (*Hedera helix*), either by weighing or with the potometer.

The results proved variable, and only by taking an average of a considerable number of experiments were figures of any sort of value obtained. For *Prunus* the average transpiration-rates in light and darkness are as 132 : 100; for ivy the figures are 136 : 100.

"*On Dimensions of Chromosomes considered in Relation to Phylogeny.*" By Prof. J. B. Farmer, F.R.S., and L. Digby.

"*The Process of Calcification in Enamel and Dentine.*" By J. H. Mummery.

Although much has been written on the calcification of teeth, the actual mode of deposition of the lime salts has been very little investigated. The author shows that both in dentine and enamel the lime salts are deposited in the globular form, despite the chemical composition of the finished tissues.

This fact is probably due to preponderance of carbonates in young tissues, as lime salts are not deposited in globular form in colloid substances when phosphates are in excess.

In drawing attention to the large part played by physical processes in calcification, the dialysis of lime salts and their deposition as calcospherites is shown in osmotic growths in chemical solutions. A repetition of some experiments of Rainey and Harting on the production of calcospherites shows that two typical forms are found in gum and in albumen, the radial and the concentric. The radial form is especially noticeable in the calcifying shell of crustacea.

It is seen that the typical form in dentine is the concentric, this structure being visible in the deeper parts of the forming dentine, the calcospherites when first deposited being clear and apparently structureless.

The lamellæ of dentine are seen to be due to extension of the elements of the calcospherites. In enamel the typical form is "radial," these calcospherites being clear and generally of an oval form in human enamel, but where undergoing disintegration they show radial splitting.

They are best seen in the enamel of marsupials where there is an abundant organic basis, and the spherites which are spherical in these animals are found lying between the laminæ, into which the enamel breaks up in teazed preparations, in all stages of disintegration.

In man they are found nearer the forming surface and immediately beneath the enamel organ, many having a diameter four times that of the enamel prism. It is shown that the sheath of Neumann has an independent existence apart from the fibril, and a study of the shell of Brachiopoda shows a similar acid-resisting membrane surrounding the tubes containing the protoplasmic prolongations from the mantle.

"*The Optimum Temperature of Salicin Hydrolysis by Enzyme Action is Independent of the Concentrations of Substrate and Enzyme.*" By Arthur Compton.

An experimental inquiry to ascertain if variations in the concentrations of an enzyme and its substrate have any effect on the optimum temperature of the enzyme. The enzyme action investigated has been the hydrolysis of salicin by an extract of sweet almonds. It is found for an action of 15 hours' duration that the optimum temperature of the reaction remains constant at 34° C. This temperature continues to be the most favourable in experiments where the concentrations of enzyme and substrate have been varied, either separately or together. The optimum temperature of the enzyme in question is, therefore, independent alike of the concentration of the substrate and of the concentration of the enzyme.

"*The Ratio between Spindle Lengths in the Spermatocyte Metaphases of Helix Pomatia.*" By C. F. U. Meek.

"*Egyptian Blue.*" By A. P. Laurie, D.Sc., W. F. P. McLintock, and F. D. Miles.

The purpose of the research is to decide the exact conditions under which the blue, manufactured and used in Egypt from the 4th dynasty to classical times, is produced, and to clear up the doubts as to its nature and constitution.

The results of the investigation are to confirm the conclusion come to by Fouqué that the blue is a double silicate consisting principally of calcium and copper, but in which these metals can be partially replaced by alkalis.

When soda, lime, and copper carbonate are heated with an excess of sand, a green glass is formed round the quartz particles at about 800° C. At about 840° the double silicate begins to crystallise out of this magma, again completely dissolving to form a green glass at 890°. The discovery of this compound by the Egyptians is doubtless due to their practice of glazing small articles carved out of sandstone with a green copper glaze.

CHEMICAL SOCIETY.

The following communications have been received during the vacation:—

261. "*The Mechanism of the Benzoin Synthesis.*" (Preliminary Note). By Gertrude Maud Robinson and Robert Robinson.

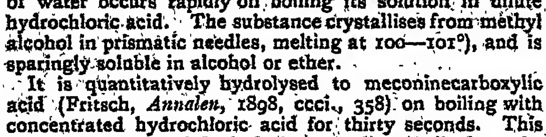
The investigation originated with the observation that cotarnine condenses with many aromatic aldehydes to form bases which are probably benzoylhydrocotarnines. With the idea of improving the yield and guided by Lapworth's well-known explanation of the benzoin synthesis, the authors attempted to prepare benzoyl hydrocotarnine (or its cyanohydrin) by the condensation of cotarnine with mandelonitrile in alcoholic solution; the products were, however, cyanohydrocotarnine and benzaldehyde. Cyanohydrocotarnine was also obtained when benzoylmandelonitrile (Francis and Dale, *Trans.*, 1909, xcv., 1404) was mixed with an equimolecular amount of cotarnine in alcoholic solution. In this case the expected benzaldehyde and benzoic acid were produced in traces only; the main products were benzoylbenzoin (m. p. 125°) and ethyl benzoate, as well as a small proportion of benzyl benzoate. A similar result was achieved when the cotarnine was replaced by sodium acetate, potassium carbonate, or sodium ethoxide. With the latter the reaction is complete, and may be expressed by the equation:—

$$2BzO\cdot CHPh\cdot CN + 2NaOEt =$$
$$= BzO\cdot CHPh\cdot COPh + Ph\cdot CO_2Et + EtOH + 2NaCN.$$

a-Cyanomeconine, $C_6H_2(OMe)_2 < \begin{matrix} CH(CN) \\ CO \end{matrix} > O$.

Opianic acid (1 mol.) and potassium cyanide (1 mol.) react in aqueous solution with the production of the potassium salt of the cyanohydrin of opianic acid. The acid is a syrup readily soluble in water, and passes very slowly into the corresponding lactone, a-cyanomeconine; the loss of water occurs rapidly on boiling its solution in dilute hydrochloric acid. The substance crystallises from methyl alcohol in prismatic needles, melting at 100—101°), and is sparingly soluble in alcohol or ether.

It is quantitatively hydrolysed to meconinecarboxylic acid (Fritsch, *Annalen*, 1898, ccci., 358) on boiling with concentrated hydrochloric acid for thirty seconds. This remarkable ease of hydrolysis must be ascribed to the recognised effect of a ring structure in increasing the reactivity of groups attached to it. The ready conversion of a-cyanomeconine to tetramethoxydiphthalyl by alkaline agents is analogous to the above production of benzoylbenzoin, and is best effected by potassium cyanide or cotarnine. The meconine hydrogen atom may be partly substituted by potassium (or cotarninium), and this intermediate substance may then condense either with itself:—



or with a molecule of cyanomeconine, in which case a further substitution of hydrogen by potassium, followed by loss of potassium cyanide, must occur before tetramethoxydiphthalyl is reached. A similar series of reactions may explain the more complicated production of benzoylbenzoin, although there are alternative methods of expressing the elimination of ethyl benzoate. The authors consider that the formation of benzoin itself is concerned entirely with the aldehydecyanohydrin in its double function as reactive cyanide analogous to ethyl iodide, and as a phenylacetonitrile with a hydrogen atom displaceable by alkali metals.

The action of potassium cyanide on mandelonitrile in boiling alcohol yields an oil which is probably benzoincyanohydrin; on treatment with sodium hydroxide in the cold, benzoin is produced. Many attempts to prepare mixed benzoins by different methods have been unsuccessful.

Incidentally, the authors have investigated the hydrolysis of acyl cyanohydrins, and find that these compounds are very well adapted for the preparation of mandelic acids. Benzoylmandelonitrile gives a good yield of benzoic and mandelic acids on prolonged boiling with concentrated hydrochloric acid, whilst on solution in sulphuric acid and subsequent dilution with water, benzoylmandelamide, $BzO\cdot CHPh\cdot CO\cdot NH_2$, is obtained. The latter crystallises from ethyl alcohol in feathery needles melting at 160—161°. Saturation of a solution of benzoylmandelonitrile (1 mol.) and ethyl alcohol (2 mols.) in dry ether with hydrogen chloride at 0°, and decomposition after twelve hours with alcohol and water, produces *ethyl benzoylmandelate*, $BzO\cdot CHPh\cdot CO_2Et$, a viscid oil boiling at 227°/20 mm., together with a relatively small quantity of benzoylmandelamide.

Benzoyl-o-nitromandelonitrile, obtained in excellent yield from o-nitrobenzaldehyde, aqueous potassium cyanide, and benzoyl chloride, crystallises from alcohol in pale yellow needles melting at 89°, and yields on hydrolysis with concentrated hydrochloric acid, benzoic and o-nitromandelic acids.

262. "*Some Derivatives of Phenanthraquinone.*" (Preliminary Note). By Kshitish Chandra Mukerjee and Edwin Roy Watson.

An investigation has been undertaken with the object of preparing derivatives with valuable dyeing properties from phenanthraquinone. Up to the present the following compounds have been obtained:—

Nitro-2 : 7-diacetoxyphenanthraquinone,—

$$C_{14}H_5O_2(OAc)_2\cdot NO_2,$$

Prepared by dissolving 2 : 7-diacetoxyphenanthraquinone in cold nitric acid (D 1·39) and plunging the containing vessel for one and a half minutes into boiling water, crystallises from a mixture of acetic acid and acetone in yellowish brown rhombic prisms, which do not melt below 290°.

Nitro-2 : 7-dihydroxyphenanthraquinone,—

$$C_{14}H_5O_2(OH)_2\cdot NO_2,$$

is obtained by hydrolysing the above acetyl derivative as a brown powder, which does not melt below 290°.

Amino-2 : 7-dihydroxyphenanthraquinone,—

$$C_{14}H_5O_2(OH)_2\cdot NH_2,$$

prepared by reducing the nitrodiacetoxyphenanthraquinone with tin and hydrochloric acid and treating the product with warm ferric chloride solution, consists of deep brown small rectangular plates, is insoluble in all ordinary organic solvents, dissolves in alkali hydroxide with a brown colour, and does not melt below 290°. Its *triacetyl* derivative, $C_{14}H_5O_2(OAc)_2\cdot NHAc$, does not melt below 295°.

2 : 7 : ?-*Trihydroxyphenanthraquinone*, $C_{14}H_5O_2(OH)_3$.—The aminohydroxy-compound is diazotised in ice-cold 10 per cent sulphuric acid, and the filtered diazo-solution on boiling precipitates the trihydroxyphenanthraquinone as a reddish brown substance, which does not melt below 290°, can be dissolved in pyridine and precipitated by alcohol, and dissolves in alkali with a brown colour. Its *triacetyl* derivative, $C_{14}H_5O_2(OAc)_3$, deposited as a reddish brown microcrystalline powder from glacial acetic acid, melts at about 280°.

2 : 7-*Diacetylaminophenanthraquinone*, $C_{14}H_6O_2(NHAc)_2$, is prepared by heating 2 : 7-diaminophenanthraquinone with acetic anhydride and fused sodium acetate at 160° for one hour in a sealed tube. It is a chocolate-brown coloured substance, readily soluble in acetic acid, sparingly so in alcohol, and does not melt below 295°.

Phenanthraquinone-2 : 7-bisazophenol,—

$$C_{14}H_6O_2(N_2\cdot C_6H_4\cdot OH)_2,$$

prepared by diazotising 2 : 7-diaminophenanthraquinone in 5 per cent sulphuric acid and coupling with phenol, crystallises from a mixture of alcohol and nitrobenzene in

brown lenticular crystals, which do not melt below 295°, and dissolve in alkali with a brown colour. The *diacetyl* derivative, $C_{14}H_6O_2(N_2 \cdot C_6H_4 \cdot OAc)_2$, crystallises from acetic acid in brick-red rhombic prisms, melting at 274°.

263. "*Some Derivatives of* 2 : 3 : 4 : 2'-*Tetrahydroxy-benzophenone.*" (Preliminary Note). By Narendra Nath Sen Gupta and Edwin Roy Watson.

This investigation has been undertaken with the object of preparing dyes of deep colour by replacing the ketonic group of the polyhydroxybenzophenones by the arrangement CR(OH). Up to the present the following derivatives of 2 : 3 : 4 : 2'-tetrahydroxybenzophenone have been prepared.

2 : 3 : 4 : 2'-*Tetrahydroxy-4''-dimethylaminotriphenyl-carbinol anhydrohydrochloride*,—

$$C_6H_2(OH)_3 \cdot C(C_6H_4 \cdot OH){:}C_6H_4{:}N(CH_3)_2Cl\ (?),$$

prepared by the action of a mixture of dimethylaniline and phosphoryl chloride on the tetrahydroxybenzophenone, is a crimson amorphous substance, melting at 184—185°, and decomposing at 200°, which dyes crimson shades on wool mordanted either with chromium or tin.

2 : 2'-*Dihydroxy*-3 : 4-*dimethoxybenzophenone*,—

$$HO \cdot C_6H_2(OMe)_2 \cdot CO \cdot C_6H_4 \cdot OH,$$

obtained by the interaction of *o*-methoxybenzoyl chloride and pyrogallol trimethyl ether in the presence of anhydrous aluminium chloride, crystallises from alcohol in yellow needle-shaped crystals, melting at 127°.

2 : 3 : 4 : 2'-*Tetramethoxybenzophenone*,

$$C_6H_2(OMe)_3 \cdot CO \cdot C_6H_4 \cdot OMe,$$

obtained by the action of methyl sulphate and potassium hydroxide on tetrahydroxybenzophenone or on 2 : 2'-dihydroxy 3 : 4-dimethoxybenzophenone, crystallises from dilute alcohol in colourless prisms, melting at 83°. Its *phenylhydrazone*, $C_6H_2(OMe)_3 \cdot C({:}N \cdot NHPh) \cdot C_6H_4 \cdot OMe$, crystallises from alcohol and melts at 153°. Its *oxime*, $C_6H_2(OMe)_3 \cdot C({:}NOH) \cdot C_6H_4 \cdot OMe$, crystallises from alcohol and melts at 166°.

The *pinacone*,—

$$C_6H_2(OMe)_3 \cdot C(C_6H_4 \cdot OMe)(OH) \cdot C(C_6H_4 \cdot OMe)(OH) \cdot C_6H_2(OMe)_3,$$

obtained by the action of zinc dust and acetic acid on the tetramethoxybenzophenone, is purified by crystallising in succession from glacial acetic acid and alcohol, and forms colourless needle-shaped crystals, melting at 185—186°.

264. "*The Constitution of Phenolphthalein and its Alkali Salts.*" By Morris Fort and Frank Leslie Barrett.

Green and Perkin (*Trans.*, 1904, lxxxv., 398) have described a method of titrating a cooled colourless solution of phenolphthalein in a known excess of potassium hydroxide with acetic acid. Using 0·5 grm. of phenolphthalein, they found 17·6 per cent of potassium hydroxide to remain unestimated by the acid, that is, the amount calculated for $C_{20}H_{15}O_5K$. The titrated solution was clear and colourless, becoming deep red and alkaline to litmus on heating, whilst a precipitate of phenolphthalein also separated out, and on again cooling these features persisted. It does not appear from the account of this work that the possible reaction between phenolphthalein and potassium acetate had been taken into account, whereas it is now found that a colourless mixture of these two substances in solution becomes red and alkaline to litmus on heating, remaining so on keeping until cold. The reaction is by no means unique, and belongs to the class of "neutral salt reactions" due to the operation of mass law (Fort, *Journ. Soc. Dyers*, 1912, xxviii., 314; 1913, xxix., 80, 120, 269; Chem. News, 1913, cviii., 1). The mere colour changes occurring on heating after titration as described have since been instanced in support of the quinonoid theory of colour (Green, *Journ. Soc. Chem. Ind.*, 1908, xxvii., 4), but now lend no support apart from the quantitative results, which appear liable to a considerable working error, being calculated from 0·65 cc., where 0·1 cc. = 3·7 per cent KOH.

Green and Perkin's experiment was therefore repeated, using also larger amounts of phenolphthalein up to 3 grms., and a series of results was obtained varying within the limits of error assigned above, for example, 16·65, 18·14, 16·10, &c. The average of ten successive experiments gave 17·54 per cent of potassium hydroxide ($C_{20}H_{15}O_5K$ requires 17·6 per cent KOH). (*a*) The amount of potassium combined with phenolphthalein as a colourless salt was also estimated directly with acetic acid, after heating and re-cooling with ice, and found to agree with the above indirect estimation. (*b*) At the same time, to decide as to the condition of phenolphthalein and the equilibrium obtaining in the red alkaline solution, the colourless solution of the monopotassium salt was closely imitated with a red solution containing fresh phenolphthalein, potassium hydroxide, and potassium acetate, and these intensely red and colourless liquids were heated side by side until of a similar intense red, behaving quite similarly on cooling with ice and titrating with acetic acid. There can therefore be little doubt as to the isomeric change taking place from the less stable colourless monopotassium salt of phenolphthalein, to the coloured quinonoid salt. (*c*) Neutral salt reactions are greatly retarded by lowering of temperature as in the titrations in (*a*) and (*b*); however, in order to determine the highest possible error from this cause, a blank experiment with phenolphthalein and potassium acetate was performed alongside (*a*) and (*b*), showing that the quantitative results are liable to be affected by the neutral salt reaction to only a small extent.

The experiments were made in duplicate, comparative throughout. The potassium hydroxide solution contained 177·184 grms. of the alkali per litre, and 25 cc. of the acetic acid were equivalent to 20·6 cc. of potassium hydroxide solution.

(*a*) One grm. of phenolphthalein and 20 cc. of potassium hydroxide solution were taken; after preparation of the colourless salt it was heated in the water-bath one hour under an air condenser, cooled with ice, and titrated to a permanent pale pink colour requiring 1·20 cc. of acetic acid = 17·5 per cent KOH. The faint pink at the end-point can be removed with a considerable excess of acetic acid, and is ascribed to the presence of potassium acetate, $C_{20}H_{15}O_5K + C_2H_4O_2 \rightleftharpoons C_2H_3O_2K + C_{20}H_{16}O_5$.

(*b*) One grm. of phenolphthalein, 9·95 cc. of potassium hydroxide solution, and 6·1968 grms. of anhydrous potassium acetate were used; the volume was as in (*a*) after the preparatory titration. The solution was heated, cooled, and titrated as in (*a*) to a pale pink: 1·2 cc. of acetic acid were required = 17·5 per cent KOH. ($C_{20}H_{13}O_5K$ = 17·6 per cent KOH).

(*c*) One grm. of phenolphthalein and 6·1968 grms. of potassium acetate were used, the volume being as in (*a*) and (*b*), alongside which the solution was heated, cooled, and titrated to a pale pink: 0·12 cc. of acetic acid was required = 1·7 per cent KOH. The intense red colour given on heating is largely retained at the ordinary temperature, but much reduced at 0°. The figure obtained from a duplicate experiment titrated at the boiling-point after an hour's heating in the water-bath was 0·29 cc. of acetic acid = 4·23 per cent KOH.

These results support the main conclusions drawn by Green and Perkin, and are in agreement with the quinonoid formulæ adopted by them for coloured phenolphthalein salts.

265. "*Complex Metal Ammonias. cis-Sulphonyldiacetato-diethylenediaminecobaltic Hydrogen Sulphonyldiacetate.*" (Preliminary Note). By Thomas Slater Price and Sidney Albert Brazier.

In his investigations of the complex cobalt ammonias, Werner has prepared a number of salts of the type [A.Co en_2]X, where A is the radicle of a dibasic acid. So far the sulphito-, carbonato-, oxalato-, and malonato-radicles have been introduced into the complex, but Werner has not been able to obtain crystalline compounds

containing the next higher homologue to the malonato-radicle, namely, the succinato-radicle, or containing the radicles of malic and tartaric acids (*Annalen*, 1911, ccclxxxvi., 81). It occurred to the authors that the introduction of the sulphur atom into the chain of carbon atoms in the acid used might lead to interesting results in this connection, and Prof. Werner having kindly informed them that he did not contemplate working with such compounds, and would leave the field open to them, an investigation was commenced, using thiodiacetic acid, $S(CH_2{\cdot}CO_2H)_2$. Definitely crystalline compounds were obtained, but the results were complicated by the fact that during the preparation, partial reduction of the cobalt compound took place, and the authors have not yet been able to characterise the compounds formed. In order to avoid this complication, the thiodiacetic acid was replaced by sulphonyldiacetic acid, $SO_2(CH_2{\cdot}CO_2H)_2$, and the compound *cis-sulphonyldiacetatodiethylenediaminecobaltic hydrogen sulphonyldiacetate*,—

$$\left[O_2S{<}\begin{matrix} CH_2{\cdot}CO{\cdot}O \\ CH_2{\cdot}CO{\cdot}O \end{matrix}{>}Co\ en_2 \right] CO_2{\cdot}CH_2{\cdot}SO_2{\cdot}CH_2{\cdot}CO_2H,$$

has been prepared.

The method of preparation was similar to that used by Werner for the corresponding malonato-compound (*loc. cit.*, p. 79). Four grms. of *cis*-carbonatodiethylenediaminecobaltic bromide were dissolved in 80 cc. of warm water, and, after cooling, 2·20 grms. of freshly prepared silver oxide were added to the solution. The mixture was well shaken for half-an-hour, and then filtered from the silver bromide into an aqueous solution of 5·63 grms. of sulphonyldiacetic acid, the proportions being 2 mols. of the acid to 1 mol. of the carbonato-base. The resulting solution, after evaporating to a small bulk on the water-bath, deposited crystals of the desired compound. One re-crystallisation from water gave the pure salt, in dull rose-coloured microscopic crystals, which are readily soluble in hot, but somewhat sparingly soluble in cold water:—

0·2687 gave 0·0767 $CoSO_4$. Co = 10·86.
0·1797 gave 16·65 cc. N_2 (moist) at 19° and 749·3 mm. N = 10·45.
0·3045 gave 0·2618 $BaSO_4$. S = 11·81.
$C_{12}H_{25}O_{12}N_4S_2Co$ requires Co = 10·91; N = 10·37; S = 11·87 per cent.

The authors are extending the investigation to other sulphur compounds and complex metal ammonias.

Extra Meeting, October 23rd, 1913.

Prof. W. H. Perkin, LL.D., F.R.S., President, in the Chair.

The Ladenburg Memorial Lecture was delivered by Prof. F. Stanley Kipping, D.Sc., F.R.S., and at the conclusion of the lecture a vote of thanks to Prof. Kipping was proposed by Prof. H. E. Armstrong, F.R.S., seconded by Prof. W. Jackson Pope, F.R.S., and acknowledged by the Lecturer.

SOCIETY OF CHEMICAL INDUSTRY.
(London Section).

Ordinary Meeting, December 1st, 1913.

Dr. W. R. Hodgkinson in the Chair.

The following paper was read and discussed:—

"*Use of Antiseptics in Increasing the Growth of Crops in Soil.*" By E. J. Russell, D.Sc. and Walter Buddin, B.A.

The action of antiseptics on the soil is shown to be complex, but the most important for the present purpose is that the micro-organic population of the soil is very considerably simplified. The higher forms of life are killed when sufficient antiseptic is added, and the bacteria are greatly reduced in numbers.

If the antiseptic is volatile or easily removed from the soil a remarkable result is obtained shortly after it has gone. The bacterial numbers do not remain low, but they begin to rise and finally attain a level much exceeding that of the original soils. Simultaneously there is an increase in the rate of ammonia production in the soil; the evidence shows that this is the direct result of the increased numbers of bacteria. The increased ammonia production, however, does not set in if a large amount of ammonia and nitrate is already present in the soil.

This increased production of ammonia induces a larger crop growth than in the untreated soils; antiseptics, therefore, tend to have the same action as nitrogenous fertilisers and could be used to supplement them in practice.

The antiseptics also have more or less effect on disease organisms present in soils. These tend to be very prevalent under certain conditions of horticultural and agricultural practice, and their destruction is not effected by any of the methods ordinarily in use. Large growers are now using steam, and this is proving very effective; the treatment costs about 1s. a ton. Chemical treatment is at present less effective, but it appears capable of much improvement and of being finally carried out at less cost per ton. The requirements are that the antiseptics should be destructive to disease organisms, pests, and organisms detrimental to the ammonia producing bacteria, that it should be capable of being removed from the soil either by volatilisation, oxidation, or decomposition, and that it should be convenient in application, and should not be absorbed too readily by the soil, or proper distribution cannot take place. To be a commercial success it must be cheap and capable of being turned out to standard. Of the various compounds tried during the last three years, formaldehyde is the best, then comes pyridene, and then cresol, phenol, carbon disulphide, toluene, and others. None of these are as good as steam, but the subject is yet in its infancy, and there is no reason to doubt that suitable antiseptics will yet be found.

SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

Ordinary Meeting, December 3rd, 1913.

Mr. Leonard Archbutt, President, in the Chair.

Messrs. John Joseph Eastick and J. F. Millar were elected Members of the Society.

Certificates were read for the first time in favour of Messrs. Rowland Holliday Ellis, "Lynwood," Thorpe Road, Selby, and Armand de Waele, "Rosemead," Sidney Road, Staines, Middlesex.

Certificates were read for the second time in favour of Messrs. Alan Milsom Bailey, Arthur Leslie Barton, Thomas Sidney Haines, and Arthur George Abraham Miller.

The following papers were read and discussed:—

"*Sulphuretted Hydrogen from Artificial Graphite.*" By W. H. Woodcock and Bertram Blount.

A sample of massive graphite manufactured by Dr. Acheson possessed the unusual property of evolving sulphuretted hydrogen when broken or rubbed. Investigation showed that this property was due not to occluded gas, but probably to the presence of a sulphide of the type of aluminium sulphide, which is decomposed on removal of the protective covering of graphite by contact with moist air.

"*Determination of Strychnine in the Presence of Quinine.*" By Charles Simmonds.

Strychnine can be accurately separated from quinine by precipitation as ferrocyanide in strongly acid solution, pro-

vided that certain conditions are observed as regards the proportions of acid and precipitant. The paper describes the requisite conditions, with experiments.

"*Rate of Liberation of Hydrocyanic Acid from Linseed.*" By S. H. Collins and H. Blair.

Linseed contains a cyanogenetic glucoside and an enzyme, which under certain conditions liberate hydrocyanic acid. The rate of liberation of hydrocyanic acid is modified by acids, alkalis, salts, poisons, digestive extracts, heat, moisture, other foods, mechanical condition, &c. Under practical conditions of feeding, dry linseed seems fairly safe, but linseed mash or soup needs to be prepared with care, under strict conditions. Insufficient heat, improper mixing, and lumpiness produce a linseed mash which is not safe for feeding calves.

"*Composition of Palm Kernel Oil.*" By George Davidson Elsdon.

The author, in continuation of his work on alcoholysis (*Analyst*, 1913, xxxviii., 8) has examined palm kernel oil with the idea of finding some method of distinguishing it from cocoanut oil. No intrinsic differences have been found, and those which do exist are not sufficently great to form the basis of a method for differentiation of the oils. The composition of palm kernel oil is given.

"*Estimation of Sulphur in Rubber.*" By Henry P. Stevens.

Confirmation is given of the loss of sulphur during the oxidation of rubber products with nitric acid. The sulphur or sulphur product given off with the vapours may be retained by passing through solutions of caustic alkalis or nitric acid. For general purposes of analysis it is sufficient to carry out the decomposition in a large flask fitted with a Young's fractionating column, or in a large Kjeldahl flask provided with a 5 inch surface condenser fitting snugly into the neck. The figures for a large number of sulphur estimations are given in confirmation of the above.

"*The Insoluble Bromide Test for Drying Oils.*" By John A. L. Sutcliffe.

The author has studied the influence of varying conditions upon the percentage of insoluble brominated glycerides obtained from linseed oil. A standard process is recommended, and the results obtained from linseed oils have been plotted as a curve against the iodine value. This curve is a straight line, of which the equation is:—
Per cent of bromides = (0·63 iodine value) − 78.

NOTICES OF BOOKS.

Practical Science for Engineering Students. By H. Stanley, B.Sc. (London and Bristol), F.I.C. London: Methuen and Co., Ltd. 1913.

Although intended primarily for the use of students in evening schools who have had some previous training in elementary science, it seems probable that this book might advantageously be adopted for rather different purposes. If supplemented by a certain amount of theoretical work it would give boys in secondary schools a thoroughly practical training in general physics, and also its clearness and conciseness should make it useful for revision work for candidates for examinations. The experiments described are such simple quantitative ones as can readily be performed without complicated or expensive apparatus. They are arranged in five sections on Heat, Mechanics, Magnetism and Electricity, Miscellaneous Experiments, and Materials respectively, but each section is independent of the others and the order in which they are taken is quite optional. The section on materials contains a few notes on some substances met with in engineering practice, *e.g.*, iron, cement, common acids, &c., and is intended rather to stimulate the student's intelligent curiosity than to satisfy it. Many problems and examples are given for calculation, and in all cases excellent schemes for the tabulation of results are provided.

Chemical German. By Francis C. Phillips. Easton, Pa.: The Chemical Publishing Co. London: Williams and Norgate. 1913.

It is very necessary nowadays for the advanced student of chemistry to be able to read German easily, and a good many text-books on scientific German have appeared recently. Many of them, however, have included at least two or three branches of science, the editors overlooking the fact that what the student usually requires is a fairly thorough acquaintance with the nomenclature of one science only. This book on chemical German is intended for the student of chemistry, and the author has wisely presupposed in his readers a knowledge of the elements, both of the language and the science. Such special points as the nomenclature of compounds are explained in detail, and a set of exercises is provided for practice in reading. These are carefully graduated in difficulty, the first having been written specially for the book; the later ones are extracts from suitable text-books, and include some classical papers, such as that by Doebereiner on his triads and Kekulé's account of his vision of the benzene nucleus. Letters of famous chemists are also included and some short biographies. All branches of chemistry are treated, and the matter is always well chosen and interesting. Some notes are added, and occasionally, but not always, attention is called to statements in the text which later work has shown to be inaccurate. A vocabulary of words not likely to be found in an ordinary dictionary and a useful list of abbreviations are given; a few slips such as Recemkörper will want correcting in a new edition.

Vom Kohlenstoff. ("Carbon"). By Henri Le Chatelier. Translated by Hermann Barshall. Halle (Saale): Wilhelm Knapp. 1913. (Mk. 18).

This book contains the introductory course of lectures on the principles of pure and applied chemistry delivered by M. Le Chatelier at the Sorbonne. The presentation of the subject differs fundamentally from the classical method, for the author believes that the best way to put the science before the student is to discuss, first of all, the quantitative laws of chemical mechanics, and afterwards to apply them to the special cases of a few reactions. Experimental facts are described only in so far as the consideration of them is necessary for the understanding of the laws, and carbon is selected as the most suitable element for providing illustrations. Hypotheses as to the constitution of matter are not treated at all, for the author considers that the beginner derives no benefit but rather positive harm from their study, since they induce him to accept debatable views as certain truths. There is undoubtedly still room for reform in methods of teaching chemistry, and this book seems to mark a distinct advance in the right direction.

Die Verwendung der seltenen Erden. ("The Use of the Rare Earths"). By Dr. C. Richard Böhm. Leipzig: Veit and Co. 1913.

The author of this book had originally intended to publish it in the form of a series of articles in "Die Chemische Industrie," but he found it impossible to condense all his material into a sufficiently small compass and accordingly decided to expand it into a book. The applications of the rare earths are divided into two classes:—Their employment in scientific work and in technical processes. Under the heading of the first class are included short accounts of the uses of the Röntgen rays and of radiology. The second section occupies the greater part of the book, and gives a complete critical review of the application of the

compounds of the rare earths in the incandescent gas-mantle and other industries. Moreover, the very numerous suggestions which have been made for other uses are noticed and their practicability discussed. These suggestions are grouped according to the property of the compound upon which the application is based, and the systematic arrangement of the text compensates to a certain extent but not entirely for a full index.

CORRESPONDENCE.

GALLIUM IN ALUMINIUM.
QUATERNIAN SERIES.

To the Editor of the Chemical News.

SIR,—Mr. Ramage's letter in the CHEMICAL NEWS (vol. cviii., p. 280) gives information that I should have included in my paper referred to therein. Much of the work mentioned on gallium is given in Roscoe and Schorlemmer's "Treatise on Chemistry," in which Hartley and Ramage are quoted as follows:—"It occurs, for example, in a large number of iron ores, from which it passes into the iron prepared from them, so that Middlesbrough cast-iron contains as much as 1 part of gallium in 33,000 parts, and is the richest source of this element known." Its wide distribution in very minute quantities is also mentioned. Browning, in "Introduction to the Rarer Elements," cites instances of its wide distribution, and likewise mentions the work of these experimenters. It is interesting to note, nevertheless, that Boulanger and Bardet find that commercial aluminium contains 1 part of gallium in about 5900 parts, 1·7 kilogrms. of aluminium yielding 0·3895 grm. of gallium oxide.

I take this opportunity of adding a few notes. Referring to the CHEMICAL NEWS (cviii., 247), if the sets of elements are arranged vertically in the order specified, it will be seen that those containing the halogens Cl, Br, and I, alternate between the sets containing Mg, Mn, Ru, and Te, and that the sum of the secondary differences ($a+b$, or $a+b+c$ in one case) is 28 in each series containing a halogen. The remaining series give corresponding values 3·82, 7·00, 17·49, and 45·27. The following table suggests a certain degree of regularity amongst all these values:—

	0 × 3·5 = 0·0
1——	
	1 × 3·5 = 3·5
1——	
	2 × 3·5 = 7·0
3——	
	5 × 3·5 = 17·5
3——	
	8 × 3·5 = 28·0
5——	
	13 × 3·5 = 45·5
5——	
	18 × 3·5

No series has, however, been given in which $a+b=0$. I now find that two or three series are possible which fulfil this apparent requirement, and which take up some outstanding elements analogous to those already appropriated. The members for these three extra series (which may be conveniently placed in another vertical column, so that they will stand opposite the others containing Cl, Br, and I) are:—C = 12, O = 16, F = 19, Na = 23; ?? = 68·88, Rh = 102·83, Ho = 163·30, Au = 197·25; Xe = 130·77, Nd = 144·28, Os = 190·50, Tl = 204·01. There may be Tl^{I}. and Tl^{II}., differing slightly in atomic weight and chemically non-separable (see Soddy, CHEM. NEWS, cviii., 168), but it is hardly safe to assume, or even suggest as probable, that *all* the elements, especially those of low atomic weight, are thus *compounded* (using this word in its generic or general sense).

The parallelism in properties is fairly good. Oxygen has the same characteristic valency as beryllium and nickel, for example, and has a high positive magnetic susceptibility at very low temperatures (compared with such elements as manganese, chromium, palladium, titanium, and rhodium), thus in one respect linking itself up with the iron group. Rhodium resembles iron (see Mendeleeff's "Chemistry," ii., 403). Holmium (see gadolinium, previously considered) probably fits the gap beyond tellurium or iodine, when the method of classification is adopted as given in the CHEMICAL NEWS, xcix., 283. Osmium, ruthenium, and manganese are perhaps related to the halogens very much as gold, silver, and copper are related to the alkali metals, only in a kind of reverse sense.

In conclusion, I wish to thank Mr. Ramage for calling attention to the incomplete statement I made, and for the further data supplied.—I am, &c.,

F. H. LORING.

INSTITUTE OF CHEMISTRY CONFERENCE.

To the Editor of the Chemical News.

SIR,—May I, as an outsider, be allowed to remark on the opinions expressed at the recent Conference of Professors of Chemistry *re* the Institute of Chemistry.

These mostly agreed that the present conditions of entrance are too narrow, being more accessible to the University chemist, to whom entrance is in many cases comparatively easy, than to the technical man, for whereas the latter is often a technical-academic chemist and therefore more qualified for the Institute of Chemistry, the former is usually only academically trained. That whereas the Institute wish to get all properly trained chemists under their regime, the present duplication of examinations and in some cases autocratic conditions of entrance are keeping away many who would do the Institute benefit. Also that research work should be a part of chemists' training, but only after he has acquired a good groundwork of scientific knowledge, such as the taking of a degree in chemistry.

As a suggestion for your readers' opinions and those concerned may I put forward the following:—

1. That the F.I.C. should bear the same relation to the A.I.C. as the D.Sc. does the B.Sc. And whereas the D.Sc. is the highest criterion of academic qualification, the F.I.C. should stand for technical skill together with a high scale of academic groundwork of scientific knowledge and some original research.

2. That a new qualification be considered, *i.e.*, a Membership of the Institute of Chemistry (M.I.C.).

3. That the gaining of any degree in chemistry, with or without honours by day or evening "internal" work should qualify for the Membership of the Institute of Chemistry (M.I.C.). In the case of evening work, only from Institutes under the strict supervision of the Institute of Chemistry.

4. That a M.I.C. should become qualified for the A.I.C. on the acceptance of a piece of original research work by the Institute. By research should be meant every branch of independent chemical investigation, either commercial or purely academic. Care would have to be taken to prevent this research developing into a species of post-graduate work, and research work under more technical experience-gaining conditions should be encouraged, since it was pointed out that even the honours and researched academic chemist still did not necessarily ensure the right professional qualifications.

5. That the somewhat mechanical step from the A.I.C. to the F.I.C. be changed and the F.I.C. be made more analogous to the qualification for Membership of the Institute of Civil Engineers. Thus an A.I.C. would be qualified for a Fellowship after, say, three or four years continuous practice in a responsible position in the chemical profession, and that very strict attention should be paid to the consideration of the manner in which the time has been spent.

It is certain that the entrance door to the Institute must be considerably widened if it is going to admit the true technical chemists. At present a man who for any reason does not wish to spend three continuous years at least at a recognised University is almost debarred from entrance—presumably for autocratic reasons of social distinction,

Such men who are gaining actual professional or technical experience in the daytime, or part of it, and are ambitious enough to work for their degree in the evening, are, in the majority of cases probably far better qualified for entrance to the Institute, when they have taken their B.Sc., which naturally takes them longer, than those men who spend several continuous years gaining a University degree and take the A.I.C. soon after without any technical experience, and in three years automatically acquire the Fellowship. Amongst those in favour of extending the regulations so as to allow these men reasonable hope of admission, provided a qualifying general exam. be passed and that they have worked at a recognised Institute, are such authorities as Sir W. Ramsay, Prof. Kipping, and Dr. Keane, all of whom understand how the part-time and evening degree men are very badly hit by present regulations. The attitude which Sir W. Tilden takes up is typical of an attitude which the Institute must sever itself from if the majority of technical chemists are to be brought even to the state of desiring intimacy with the Institute of Chemistry. Sir W. Ramsay said that he considered that even laboratory boys who had taken their degree should be encouraged, and not kept under for the reason that they had not been sufficiently fortunate to have had the means for a University course, but Sir W. Tilden did not consider that the Institute should open its doors to even those laboratory boys who had made admirable chemists. He goes on to say:—"I do not say that you will not find extremely clever people amongst this class; the question is whether they will fairly represent professional chemistry if we help them to get into general practice; I think not, and it is on the ground of deficiency of general education I have in the past mainly felt an objection to admitting those students who come to the evening classes of many Institutions. Very many of these are most worthy, most industrious, very intelligent, but somehow I think that if we are going to build up a body comparable in social standing as well as professional rank with the great Institutions which have been referred to this afternoon, we must see that we do not admit too many of a class of persons who, whatever their other merits may be, are certainly not qualified to represent the Institute on public occasions and in the eyes of the world."

This is quite right in extreme theory, but does Sir W. Tilden think that all evening classes and part-timers are composed of laboratory boys, and that the admittance of the best of these "most worthy, most industrious, very intelligent" students necessitates them representing the Institute on public occasions and in the eyes of the world? We do not want the door opened wide so that all may flock in, but we do hope for a ray of light and hope, for at present there is almost none, and the way is so long and dreary as to not make it worth the ambition and perseverance required!—I am, &c.,

O. W. Wood.

King's College, University of London.

Literary Intelligence.—Messrs. J. and A. Churchill are about to publish the following new books and new editions:—"A Manual for Masons," by J. A. Van Der Kloes, Professor in the Science of Materials of Construction, Technical High School, Delft; revised by Alfred B. Searle. "Modern Steel Analysis," by J. A. Pickard, B.Sc., Honours London A.R.S.Sc., A.I.C., F.C.S., Carnegie Research Scholar of the Iron and Steel Institute. "The Story of Plant Life in the British Isles," by A. R. Horwood, Member of the British Botanical Society, Ecological, Conchological Societies, &c.; illustrated with seventy-three photographs. "Materia Medica, Pharmacy, Pharmacology, and Therapeutics," by W. Hale White, M.D., F.R.C.P.; 13th edition. "Elementary Practical Chemistry" (Part I.), by Frank Clowes, D.Sc.Lond., and J. Bernard Coleman, A.R.C.Sc.; Sixth Edition; with seventy-six illustrations. "The Medical Directory, 1914." "Who's Who in Science," 1914; with over 9000 Biographies.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xlvi., No. 13, 1913.

Oxidation of Nitrogen in the Electric Discharge.—A. Koenig and E. Elöd.—The authors have investigated the oxidation of nitrogen during the electric discharge, using the experimental arrangement of Fischer and Hene, and their results have led them to the conclusion that there is no warrant for regarding the oxidation as due to the activation of the oxygen. Their experiments with continuous current arcs indicate that the chemical action of the gases mixed behind the arc is due to the fact that in consequence of the active motion of the gases in the region of discharge fresh quantities of gas are always being acted upon by the discharge.

Influence of Foreign Substances on the Activity of Catalysts.—C. Paal and Arthur Karl.—The authors have already shown that when palladium is precipitated on metallic Al, Fe, Cu, Zn, Ag, Sn, or Pb, it loses its power of rendering hydrogen active, and thus hydrogenating unsaturated compounds. The metals have the same effect in the form of oxides, hydroxides, and carbonates. This is specially noticeable in the case of basic lead carbonate, which completely prevents the catalytic action of palladium precipitated on it. On the other hand, the oxide of a metal such as magnesium, which does not influence the catalytic action of palladium, increases its activity owing to its greater surface.

Ammonium Peroxides.—J. D'Ans and O. Wedig.—When dry NH_3 is led into an absolute ether solution of pure H_2O_2, cooled to -10°, clear crystals separate after a short time. If more of the gas is passed in the crystals melt, and a thick oily liquid collects at the bottom of the vessel. The ethereal layer contains NH_3 and traces of H_2O_2. The crystals first formed are NH_4O_2H. They melt and decompose at about 14°. The oily layer solidifies to a crystalline mass at about -40°, and analysis shows that its composition corresponds to the formula $(NH_4)_2O_2$ (ammonium peroxide).

New Method of Preparation of Colloidal Sulphur and Selenium.—Julius Meyer.—To prepare colloidal sulphur and selenium solutions the powdered element is dissolved in a few cc. of hydrazine hydrate, and the solution is energetically shaken. When a saturated solution has been made a syrupy dark coloured liquid is obtained. If a few drops of this solution are added to some litres of water, stirring thoroughly with selenium, a red coloured solution is obtained, and with sulphur a whitish yellow solution. The selenium solution is exceedingly stable, and can be boiled for some time without undergoing any change. It can be kept for months. When it is allowed to stand for some time a small quantity of red selenium separates, but it disappears on shaking. The sulphur solution is not so stable as the selenium solution.

Isomeric Forms of Anhydrous Sodium Acetate.—D. Vorländer and Otto Nolte.—Two isomeric forms of anhydrous sodium acetate exist. The one which appears first when the amorphous melt cools may be called I., and the one appearing at a lower temperature II. The first is monoclinic and the second rhombic. II. passes over into I. at 198°; the transition is enantiotropic. When sodium acetate crystallises from absolute ethyl or methyl alcohol the salt II. is always obtained, whichever salt was originally dissolved. This salt II. is a very good condensation agent; it abstracts water more rapidly than I.

MEETINGS FOR THE WEEK.

SATURDAY, 27th.—Royal Institution, 3. (Christmas Lectures, adapted to a juvenile auditory). "A Voyage in Space," by Prof. H. H. Turner, D.Sc., F.R.S., &c.

THE CHEMICAL NEWS.

Vol. CVIII., No. 2822.

THE RUSTING OF IRON IN WATER.

By W. A. BRADBURY.

Many years ago, Prof. Crace Calvert showed that bright iron rusted very quickly when immersed in Manchester tap-water, and he came to the conclusion that the carbonic acid and oxygen dissolved in the water was the cause of the rusting; the carbonic acid being the pre-disposing cause, as iron would not rust if carbonic acid was absent.

Since these experiments were made, a very considerable amount of attention has been given to the question, and many eminent authorities support Prof. Crace Calvert's conclusions.

As any experiments bearing on this subject have a certain value I wish to record the following:—Two flasks were filled with well boiled Manchester tap-water, and some coils of bright iron binding wire added; the flasks were then corked. No rust formed. A coil of bright iron wire, placed in water as drawn from the tap, soon became coated with rust, and the water then gave a blue coloration when tested with potassium ferrocyanide.

An experiment was arranged as per sketch, Fig. 1. A small flask containing water and iron wire was placed in a beaker, and water filled into the beaker until it rose partly up the neck of the flask. A small beaker was then wedged into position, so that the mouth of the small beaker was sealed. In a few hours the iron began to rust, and the rusting continued until a very fair amount was formed; the water gradually rose in the covering beaker until about one-fifth of the space was occupied by the water. The rust was filtered off from the water; a portion of the filtrate tested with potassium ferricyanide gave a blue coloration showing the presence of ferrous iron. The remaining portion of the filtrate was boiled; it turned rusty-looking, and gave a deposit of oxide of iron; this was filtered off, and the filtrate was found to be free from iron.

The dissolving of iron by carbonic acid should give rise to an evolution of hydrogen,—

$$Fe + 2H_2CO_3 = FeH_2(CO_3)_2 + H_2$$

Apparatus arranged as per sketch, Fig. 2, using Manchester water and bright iron wire. In about five hours the water turned rusty-looking, but no gas had collected. The action was allowed to continue for a week, the formation of rust then seemed to cease. No gas had collected. In this case only a very slight amount of bicarbonate of iron was contained in the water.

To account for the absence of hydrogen in the collecting tube we must assume that nascent hydrogen combines with a portion of the oxygen dissolved in the water, and the rusting ceased when all this oxygen was used, and the water being sealed from atmospheric action no further supply of oxygen could be obtained.

As in the act of rusting the carbonic acid is again liberated, there should be a time when the liberated carbonic acid should act upon the iron and hydrogen be given off, all the oxygen having been used up.

As the amount of carbonic acid dissolved in water is usually very small, it may be that the hydrogen liberated in the final reaction is absorbed in the water, and hence its absence in the collecting tube.

To further test these points carbonic acid was passed into water for about fifteen minutes (170 cc. water), the arrangement, Fig. 2, being again used. After twenty-four hours action the iron remained perfectly bright; a portion of the water tested with potassium ferricyanide showed the presence of ferrous iron. No gas had collected. Water was added to make up for the portion tested, and the experiment continued for six days. At the end of the sixth day the iron was still bright, and a bubble of gas had collected in the bend of the delivery tube. At the end of fourteen days the iron was still bright, and the delivery tube was filled with gas (about 5 cc.).

About three-fourths of the water, which was perfectly colourless and clear, was boiled; a large deposit of oxide of iron formed, consisting of both ferrous and ferric oxides. This was filtered off, and the filtrate evaporated to a small bulk; no further deposit occurred, and the liquid remained perfectly colourless on addition of potassium ferrocyanide.

The remaining one-fourth of the water with the iron still immersed in it was exposed to the atmosphere; in about two hours the water turned rusty-looking.

In this experiment we have a large amount of iron passed into solution, and the iron remaining perfectly bright, and the water remaining perfectly clear. This can only be due to the nascent hydrogen formed by the solution of the iron in carbonic acid, and no gas collected until all the oxygen dissolved in the water had been eliminated

Fig. 1.

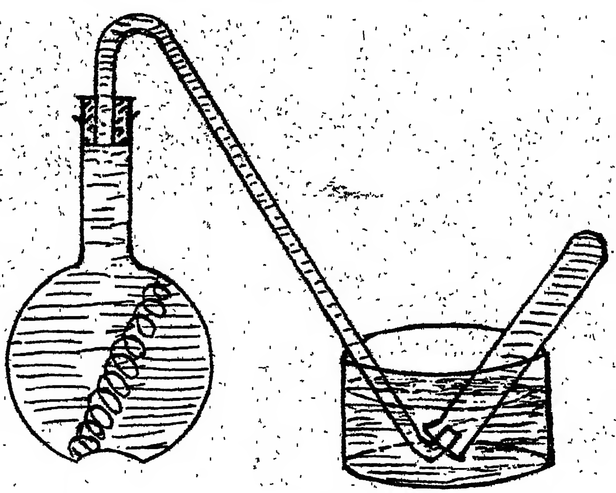


Fig. 2.

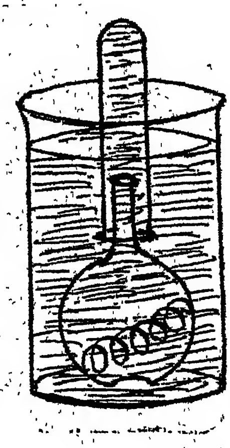


Fig. 3.

The carbonic acid in the water was then present in sufficient quantity to give off more hydrogen, by its action on the iron, than the water was able to absorb.

The continuous rusting which goes on when the vessels are left open to the atmosphere is due to the ease with which oxygen from the atmosphere is absorbed by the water.

These experiments confirm the view that the rusting of iron in water is due to the dissolved oxygen and carbonic acid. They also show that the dissolved oxygen is utilised in two ways:—(1) It combines with the nascent hydrogen to form water, and (2) it decomposes the bicarbonate of iron to form rust, and however much rusting goes on there always remains in solution some bicarbonate of iron.

There seems to be a general impression that magnesium chloride in water has a strong corrosive action upon iron. It has been stated that magnesium chloride, *even in the cold*, acts in the following way:—

$$MgCl_2+Fe+2H_2O=Mg(OH)_2+FeCl_2+H_2.$$

To 500 cc. of well-boiled water 25 cc. of a saturated solution of magnesium chloride was added, and bright iron wire placed in the flask, using the arrangement Fig. 3. No signs of rust appeared, and not a bubble of gas collected after fifteen days action. On testing the solution with potassium ferrocyanide no blue coloration formed.

The arrangement, Fig. 2, was again used with boiled water and magnesium chloride. The solution was kept just short of ebullition by heating the flask on a sand-bath. After twenty-four hours heating neither rust nor gas had formed. The solution was evaporated to a small bulk, and it was found to be free from either ferrous or ferric iron.

This experiment was repeated, using a saturated solution of magnesium chloride. No gas formed, no iron dissolved. Magnesium chloride then does not act upon iron, either in the cold or heat at atmospheric pressure.

Dr. J. Grossman, in a paper read before the Society of Chemical Industry in Manchester, says that in the presence of carbonate of lime which most natural waters contain, magnesium chloride does not corrode iron when heated to a pressure of 200 lbs. or 300 lbs. per square inch.

We must therefore conclude that magnesium chloride has not the deleterious action upon iron which is usually ascribed to it.

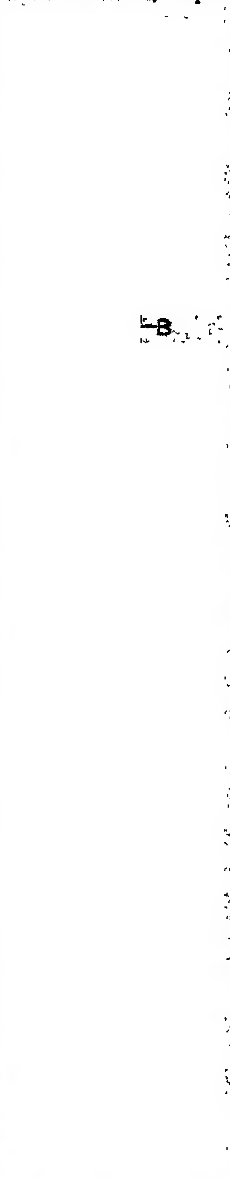
ON EXTRACTION WITH LIQUEFIED GASES AND THE AMMONOLYSIS* OF HYDRAZINE SULPHATE.

By FRITZ FRIEDRICHS.

IN connection with the choice of a solvent for use in extraction two considerations are of importance:—First, the relative solubility of the substances to be separated, and, second, the ease with which the solvent may be recovered without loss and without decomposition of the extract or of the residue. Since the removal of the solvent is usually effected by evaporation, a solvent with the lowest possible boiling-point would normally be preferable, especially when the material to be extracted decomposes at relatively low temperatures or possesses a high vapour tension. This leads at once to the application of liquefied gases in extraction in case the usual solvents cannot be readily recovered after the operation is complete.

The reason that such comparatively inexpensive gases as ammonia, sulphur dioxide, hydrogen sulphide, methylamine, &c., have not found more frequent application as extracting media in scientific and industrial work lies in the fact that the solvent power of these substances, with the exception of ammonia, has not yet been thoroughly investigated, and, further, that suitable apparatus for the purpose has not yet been designed. Various extractions, to be discussed in more detail later, have already been carried out by A. W. Browne, T. W. B. Welsh (*Journ. Am. Chem. Soc.*, 1911, xxxiii., 1728), and A. E. Houlehan (*Ibid.*, 1911, xxxiii., 1734), but the apparatus employed has not yet been completely developed for general use. The author of the present paper, in undertaking the continuation of the work, has consequently devised, on the basis of the work already done, the apparatus shown in the accompanying sketch.

The apparatus consists of three parts—(1) the extraction apparatus proper, D, (2) the container C, for the substance to be extracted, suspended in D from three glass projections, and (3) the condenser B, which is carefully ground to fit D. The extraction apparatus is modelled after the Landsiedl device, except that the bulb F is provided with a small syphon and with a stopcock, G, through which the extract may be drawn off, and that the entire apparatus is insulated by means of a vacuum jacket. Between this jacket and the inner part of the apparatus a small quantity of the refrigerant may be introduced. The condenser is of the screw type (*Zeit. Angew. Chem.*, 1910, xxiii., 2425), the screw itself constituting a receptacle for the refrigerant, and is, like the extraction apparatus, surrounded by a vacuum jacket. In order to permit free delivery of the condensate and free return of the vapours the condenser is equipped with a special device clearly shown in sketch. It is to be noted that the glass tubes passing through the vacuum jackets are in each case so constructed as to permit thermal expansion or contraction without breaking the apparatus. The upper part of the condenser is provided with an inlet tube for the gas to be liquefied, which is obtained from some convenient source, either a cylinder or a gas generator, and which is suitably purified and dried (in the case of ammonia, for example, by means of a long tube filled with sodium wire). It is advisable also to connect the condenser with a mercury manometer, which serves the double purpose of indicating the pressure in the apparatus and of acting as a safety outlet.



For the gases already named, solid carbon dioxide and ether may be used as the refrigerant, while for gases with lower boiling-points, such as oxygen or methane, liquid air may be employed. When liquid air is used it is advisable to introduce first a small amount of ether into the apparatus, and then slowly to add the liquid air, in order to minimise danger of breaking the apparatus. In order to obtain still lower temperatures in the condenser, the screw may be connected with an air-pump, and the refrigerant caused to evaporate under reduced pressure.

The apparatus just described has been found to serve admirably in a research upon the ammonolysis of hydrazine sulphate. As already shown by Browne and Welsh, hydrazine sulphate is decomposed by liquid ammonia into free hydrazine and ammonium sulphate in accordance with the equation:—

$$N_2H_4.H_2SO_4+NH_3 \rightleftharpoons (NH_3)_2.H_2SO_4+N_2H_4.$$

The reaction is, moreover, to be regarded as reversible, inasmuch as Lobry de Bruyn has already shown that free hydrazine can liberate ammonia from ammonium sulphate (*Rec. Trav. Chim.*, 1896, xv., 179). Since ammonium sulphate—or rather, in accordance with the hitherto unpublished experiments performed by Mr. L. J. Ulrich in the Cornell University Laboratory, the triammonate of ammonium sulphate—is entirely insoluble (Franklin and Kraus, *Am. Chem. Journ.*, 1898, xx., 820) in liquid ammonia, while hydrazine is comparatively soluble, the employment of an excess of ammonia during the extraction displaces the equilibrium toward the right, with the result that quantitative ammonolysis takes place. It was therefore to be expected, as Browne, Welsh, and Houlehan have already intimated, that anhydrous hydrazine might be conveniently prepared by this method.

The hydrazine sulphate used in the following experiments was obtained by precipitation with alcohol from an aqueous solution of a sample of the salt previously purified by four-fold re-crystallisation. This product was repeatedly washed with alcohol, and was finally dried in a desiccator. A weighed sample of this pure white salt was introduced into the vessel C in a Schleicher and Schüll extraction thimble, and after opening the stopcock G, the air was driven from the apparatus by means of ammonia. By filling the tube between the stopcock G and the bulb F with mercury, which is of course a good conductor of heat, it was found possible to supply automatically an amount of heat sufficient to effect continuous evaporation of the liquid ammonia in F. After the salt had become pretty well saturated with ammonia at room temperature, solid carbon dioxide and ether were introduced into the jacket of the extraction apparatus and into the condenser screw A. Ammonia was at once condensed, and the extraction began to take place. During this operation the bulk of the salt increased to such an extent that during the earlier experiments the paper thimble, and on one occasion even the vessel C, burst, while in another case C became clogged so as to necessitate interruption of the experiment. It was then found that these difficulties could be readily avoided by placing glass-wool in the thimble with the salt, by supporting the thimble upon a porcelain Witt plate, and by inserting several short pieces of glass tubing between the thimble and the walls of C. When the bulb F had become about three-fourths filled with liquid, the valve of the ammonia cylinder was closed. The operation of the apparatus was then entirely automatic, and was surprisingly smooth and uniform, as could be observed from the manometer. As the temperature of the gas that rises from F to the condenser is never higher in the apparatus than the boiling-point of liquid ammonia ($-33{\cdot}45^{\circ}$ under atmospheric pressure) or of the liquid ammonia solution, the consumption of carbon dioxide is relatively low. During the ammonolysis experiments, for example, it was found necessary on the average to fill the condenser screw from three to four times for each extraction. After the extraction had been completed the apparatus was allowed to warm up and the gas to escape through the safety outlet. The extract was then drawn off by opening the stopcock G. When it was desired to measure the amount of the extract directly it was, of course, necessary to rinse out the bulb F with liquid ammonia. The vessel C containing the residual ammonium sulphate combined with considerable amounts of ammonia in the form of an ammonate was now removed, was left in a desiccator over sulphuric acid until free from ammonate ammonia, and was weighed. The results obtained in several typical experiments are summarised in the accompanying table.

In Experiments 2, 3, and 4 the presence of hydrazine in the residue could not be detected with the aid of Fehling's solution, nor could the presence of sulphuric acid be shown in the extract. In Experiment 1 several hard lumps of salt containing a considerable amount of hydrazine were found at the bottom of the thimble, indicating that the extraction was not in this case complete. This first experiment was therefore left out of account in calculating the average. The loss of hydrazine was occasioned by the necessity of rinsing out F with liquid ammonia.

No. of expt.	$N_2H_4.H_2SO_4$ used. Grms.	$(NH_3)_2.H_2SO_4$. Obtained. Grms.	Calculated. Grms.	Percent of theory.	NH_4. Obtained. Grms.	Per cent of theory
1	2·082	2·14	2·11	101·4	—	—
2	2·366	2·42	2·43	99·6	0·529	90·6
3	4·688	4·79	4·76	100·6	0·817	95·9
4	8·377	8·52	8·50	100·2	—	—
Average of expts. 2, 3, and 4 ..				100·1		

From these experiments it is evident, as was to be expected, that the ammonolysis may be considered to proceed quantitatively under the prevailing conditions. It is further to be concluded that it should be possible without difficulty to prepare anhydrous hydrazine in larger amounts by this method. For this purpose it would, of course, be advisable to substitute an apparatus built of iron for that of glass. It would then be possible to use ice as the refrigerant, as the apparatus would readily bear a pressure of 4·2 atmospheres. The greater solvent power of liquid ammonia at the higher temperature would undoubtedly be of advantage. Experiments in this direction are now in progress.

It is hoped that this illustration of the application of liquefied gases as extraction media will call the attention of other investigators to this field of work, and that the apparatus described herewith may be of service in carrying out further experiments.

In conclusion the author wishes to express his gratitude to Prof. A. W. Browne, who has suggested the present investigation, and to the firm of Grenier and Friedrich, Stützerbach, Germany, by whom the apparatus has been constructed.—*Journal of the American Chemical Society*, xxxv., No. 3.

THE AMMONIA SYSTEM OF ACIDS, BASES, AND SALTS.*

By EDWARD C. FRANKLIN.

(Concluded from p. 298).

9. *Ammono Salts Analogous to the Zincates, Aluminates, Plumbites, &c.*—Among the phenomena with which the student of chemistry early becomes familiar is the solubility of certain metallic hydroxides, such as the hydroxides of aluminium, lead, and zinc, in solutions of the alkali hydroxides, and he soon learns to write confidently the equations—

$$Al(OH)_3+3KOH=Al(OK)_3+3H_2O,$$
$$Zn(OH)_2+2KOH=Zn(OK)_2+2H_2O,$$
$$Pb(OH)_2+2KOH=Pb(OK)_2+2H_2O,$$

as representing the reactions which take place. As a matter of fact, the composition of the compounds thus formed is still a matter of doubt (Hantzsch, *Zeit. Anorg. Chem.*, 1902, xxx., 289; Wood, *Journ. Chem. Soc.*, 1910, xcvii., 878).

The observations that certain metallic salts in solution in liquid ammonia, when treated with potassium amide, give precipitates which re-dissolve on adding the precipitant in excess, suggested the possibility of preparing the ammonia analogues of the substances supposed to be present in the alkaline solutions mentioned above. The results of work in this direction have been highly satisfactory; for most of the compounds so far obtained are beautifully crystalline and of sharply definite composition; results which are in striking contrast to the properties of the analogous oxygen compounds in this respect.

After the earlier unsatisfactory attempts to prepare a potassium ammonoplumbite (Franklin, *Journ. Am. Chem.*

* From *American Chemical Journal*, xlvii., No. 4.

Soc., 1905, xxvii., 843), the first representative of this class of compounds to be obtained, namely, potassium ammonozincate, was successfully prepared by F. F. Fitzgerald (*Journ. Am. Chem. Soc.*, 1907, xxix., 660); Franklin, *Ibid.*, 1907, xxvii., 1274).

Potassium Ammonozincate, $Zn(NHK)_2.2NH_3$.—In view of the fact that metallic zinc dissolves in aqueous potassium hydroxide with the evolution of hydrogen, it was hoped that analogously a pure solution of potassium ammonozincate would be formed by the action of a liquid ammonia solution of potassium amide on the metal. Fitzgerald found that the reaction represented by the equation $Zn+2KNH_2 = Zn(NHK)_2+H_2$ takes place readily enough, especially if the zinc is alloyed with a little platinum. Because, however, of the slight solubility of the salt in liquid ammonia, its separation from the excess of zinc is a matter of considerable difficulty.

A second method by which potassium ammonozincate has been successfully prepared is by treating zinc amide (Fitzgerald, *loc. cit.*), obtained by the action of ammonia gas on zinc ethyl, with a liquid ammonia solution of potassium amide. The amorphous insoluble zinc amide formed by the action of ammonia on zinc ethyl is converted into a mass of well crystallised potassium salt when allowed to stand overnight in contact with an excess of a solution of potassium amide. The reactions involved are represented by the equations—

$$Zn(C_2H_5)_2+2NH_3 = Zn(NH_2)_2+2C_2H_6$$

and

$$Zn(NH_2)_2+2KNH_2 = Zn(NHK)_2.2NH_3.$$

Finally, and most conveniently, the salt has been prepared by the action of an excess of potassium amide in solution in liquid ammonia directly upon ammonated zinc iodide, as represented by the equation—

$$ZnI_2.4NH_3+4KNH_2 = Zn(NH_2)_2.2KNH_2+2KI+4NH_3.$$

The crop of well crystallised slightly soluble zincate thus formed is easily obtained pure by washing with liquid ammonia to remove the potassium iodide formed, together with the excess of potassium amide. Potassium ammonozincate dissolves readily in liquid ammonia solutions of ammonium nitrate (that is to say, in nitric acid). It is energetically hydrolysed by the action of water; even short exposure to the action of the moisture of the atmosphere produces a superficial sticky layer on the clear dry crystals. It is not explosive. When heated *in vacuo* potassium ammonozincate remains intact up to 160°; as the temperature is increased beyond this point, the substance melts and gives off ammonia. Heating the salt for some hours at temperatures between 250° and 300° gave a residue of approximately the composition represented by the formula $Zn(NHK)_2.\frac{1}{2}NH_3$.

Potassium Ammonostannate, $Sn(NK)_2.4NH_3$ and $Sn(NK)_2.NH_3$.—The preparation of a pure crystalline salt of the composition represented by the first formula was accomplished by Fitzgerald (*Journ. Am. Chem. Soc.*, 1907, xxix., 1694) by the action of potassium amide in excess on a liquid ammonia solution of stannic iodide. The reaction takes place in accordance with the equation $SnI_4+6KNH_2 = Sn(NK)_2.4NH_3+4KI$ (stannic iodide forms a white addition product with ammonia), and since the salt formed is crystalline and but slightly soluble in ammonia, it is easily washed free from potassium iodide and excess of potassium amide. Potassium ammonostannate is soluble in liquid ammonia solutions of ammonium iodide; that is to say, it is decomposed and dissolved by hydriodic acid in liquid ammonia solution. It is vigorously attacked and decomposed by water. Heated in contact with the air it takes fire and burns with brilliant incandescence. It is not explosive. When heated *in vacuo* it loses 3 molecules of ammonia and is converted into a brick-red powder of the composition represented by the formula $Sn(NK)_2.NH_3$.

It is most interesting to point out the analogies between these two ammono compounds and the correspondin oxygen salts. A formula for potassium metastannate cannot be given corresponding to the formula $Sn(NK)_2.4NH_3$, but if the nitrogen compound be given any one of the formulæ $(NH_2)_2:Sn:(NHK)_2.2NH_3$, $(KNH)_2:Sn:(NHNH_4)_2$, or $Sn(NH_2)_4.2KNH_2$, then it is easy to write the analogous formulæ $(HO)_2:Sn:(OK)_2.2H_2O$, $(KO)_2:Sn:(OH_3O)_2$, and $Sn(OH)_4.2KOH$ for the oxygen compound (*cf.*, Bellucci and Parravano, *Zeit. Anorg. Chem.*, 1905, xlv., 142). If Bellucci's contention that the formula for the ordinary trihydrate of potassium metastannate is to be written $K_2Sn(OH)_6$, then analogously the formula for the ammonostannate may be written $K_2Sn(NH_2)_6$. Corresponding to the formula, $K_2SnO_3.3H_2O$, usually given to the aquo salt, the formula $K_2Sn(NH)_3.3NH_3$ may be written for the ammono salt.

The similarity of the behaviour of these two compounds when heated is also noteworthy, for just as the aquo salt loses 3 molecules of water, so the ammono salt loses 3 molecules of ammonia, to form compounds which in the one case may be given either of the formulæ K_2SnO_3 or $O:Sn:(OK)_2$, and in the other any one of the three formulæ $K_2Sn(NH)_3$, $NH:Sn:(NHK)_2$, or $Sn(NK)_2.NH_3$ (Note 10).

Potassium Ammonocadmiate, $Cd(NHK)_2.2NH_3$ (Note 11).—When a solution of potassium amide is added to ammonated cadmium iodide or nitrate, an amorphous or microcrystalline insoluble product is obtained which analysis shows to be a cadmium salt corresponding in composition to the zinc salt described above (Note 12).

Potassium Ammonoplumbite, $PbNK.2\frac{1}{2}NH_3$, $PbNK.2NH_3$, and $PbNK.NH_3$.—The attempts mentioned above to isolate the product of the action of potassium amide on lead imide have recently been renewed in this laboratory and with entire success (*Journ. Phys. Chem.*, 1911, xv., 509). It has been shown that the reaction between the ammono base and the amphoteric imide is to be represented by the equation $PbNH+KNH_2 = PbNK+NH_3$. The salt possesses conspicuous crystallising power and is obtained from very concentrated solutions in the form of beautifully developed colourless transparent crystals, having the composition represented by the formula $PbNK.2\frac{1}{2}NH_3$. At 40° below zero, if the pressure is sufficiently low, the salt effloresces, losing one-half a molecule of its ammonia. At 60° it loses an additional molecule of ammonia, and is converted into a dark brown mass still showing the form of the original crystals. The product thus formed, $PbNK.NH_3$, does not further lose ammonia when heated to a temperature of 140°. At somewhat higher temperatures the compound explodes. It also explodes violently when brought into contact with water or dilute acids, and occasionally even on simple exposure to the atmosphere.

When a solution of ammonium iodide in liquid ammonia is gradually added to a solution of potassium ammonoplumbite, a brown precipitate of lead imide is first formed, which with further addition of ammonium iodide is converted into a white ammonobasic lead iodide (see Section 10). On adding still further quantities of ammonium iodide, the basic lead salt dissolves to form lead iodide. The equations representing these reactions are as follows:—

$$PbNK+NH_4I = PbNH+KI+NH_3,$$
$$2PbNH+NH_4I = NH_2PbNHPbI.NH_3,$$

and

$$PbNPbI.2NH_3+3NH_4I = PbI_2+6NH_3.$$

Conversely, the gradual addition of potassium amide to a solution of lead iodide brings about the successive formation of ammonobasic lead iodide, lead imide, and potassium ammonoplumbite.

The analogy between these reactions and those which result from the gradual addition of nitric acid to a solution of potassium plumbite, and the inverse reactions which accompany the gradual addition of potassium hydroxide solution to a solution of lead nitrate, are so obvious as to require no statement in detail.

Potassium Ammonocuprite, $CuNK_2 2\frac{1}{2}NH_3$ and $CuNK_2.NH_3$.—When cuprous nitride, obtained in the manner described by Fitzgerald (*loc. cit.*), is treated with a liquid ammonia solution of potassium amide, a salt of the composition represented by the first of the above formulæ is formed, which, because of its extreme solubility, has so far been obtained only in an approximate degree of purity (experimental results not published). At low temperatures the salt separates from very concentrated solutions in the form of colourless crystals, which readily part with one and one half molecules of their ammonia of crystallisation. One molecule of ammonia is retained up to 200°, above which temperature the heating has not been carried.

The formation of potassium ammonocuprite is represented by the equation $Cu_3N+6KNH_2=3CuNK_2+4NH_3$.

Potassium Ammonothallate, $TlNK_2.4NH_3$, $TlNK_2.2NH_3$, and $TlNK_2.1\frac{1}{3}NH_3$.—Black thallium nitride dissolves in liquid ammonia solutions of potassium amide to form a clear yellow solution, from which, on cooling the not too dilute solution, a crop of beautiful yellow crystals separates. Dried *in vacuo* at −40°, these crystals retain their colour and have been shown to have the composition represented by the formula $TlNK_2.4NH_3$ or $TlNH_2.2KNH_2.2NH_3$ (experimental results not yet published). On warming up to laboratory temperature the salt takes on a lighter colour, loses 2 molecules of ammonia, and is converted into a compound which is represented by the formula $TlNK_2.2NH_3$ or $TlNH_2.2KNH_2$. When heated to 100° the latter compound loses two-ninths of its nitrogen in the form of ammonia and is converted into a black mass to which the formula $TlNK_2.1\frac{1}{3}NH_3$ may be given, but which may be merely a mixture of thallium nitride and potassium amide in the proportions represented by the formula $Tl_3N.6KNH_2$. When dry, that is, when free from liquid ammonia, any one of these products explodes with violence on the slightest provocation. The yellow solution of potassium ammonothallate, when treated with a solution of ammonium nitrate, gives first a precipitate of thallium nitride, which then, on further addition of the acid, goes into solution as thallium nitrate.

10. *Ammonobasic Salts. Ammonolysis.*—As has already been shown, the reactions between ammonia and the non-metallic compounds indicated in the equations given above (p. 296) are strictly analogous to those which take place when the respective substances are treated with water, and are therefore appropriately designated as ammonolytic in order to recall their close relationship to hydrolytic reactions. These particular ammonolytic reactions proceed energetically to completion and are quite as irreversible as are the corresponding reactions which result from the treatment of the halogen compounds of the non-metals and water. Silicon chloride and the phosphorus chlorides, for example, are completely ammonolysed in contact with ammonia, just as they are completely hydrolysed by the action of water. However, just as certain well known hydrolytic reactions are reversible, so also have salts of a number of the less positive metals, when treated with liquid ammonia, been found to give basic precipitates which are increased in amount by the addition of potassium amide, and which are completely dissolved by the addition of an appropriate acid, that is to say, by the addition of an ammonium salt.

Attention was first called to the existence of such reactions by Franklin and Cady (*Journ. Am. Chem. Soc.*, 1904, xxvi., 512), who observed the formation of what they assumed to be a "basic bismuth nitrate" ("a salt related to ammonia as the ordinary basic nitrate is related to water") around a bismuth anode during the passage of an electric current through a dilute solution of ammonium nitrate in liquid ammonia.

Franklin and Kraus (*Am. Chem. Journ.*, 1900, xxiii., 299) had earlier observed the separation of a small quantity of an insoluble compound accompanying the action of liquid ammonia on mercuric chloride. It was later shown that the formation of this residue is due to the ammonolytic action of liquid ammonia on mercuric chloride (Franklin, *Journ. Am. Chem. Soc.*, 1905, xxvii., 841), as represented by the equation—

$$HgCl_2+2NH_3 \rightleftarrows NH_2HgCl+NH_4Cl,$$

and that the product is identical with the well known infusible white precipitate. The reversibility of the reaction is shown by the observation that addition of ammonium chloride to the mercuric chloride prevents the formation of the white precipitate when the mixture is treated with liquid ammonia, and by the fact that addition of sodium amide to the system represented by the above equation displaces the equilibrium to the right, while addition of ammonium chloride solution to the liquid in contact with the precipitate determines the disappearance of the latter.

In an entirely similar manner, lead nitrate, lead iodide, mercuric iodide, mercuric bromide, bismuth iodide, bismuth bromide, and stannic iodide undergo ammonolysis to a greater or less extent when treated with liquid ammonia. Although abundantly soluble in liquid ammonia no one of those salts dissolves to a clear solution unless a quantity of an appropriate ammonium salt is present.

The observations of Fitzgerald (*Journ. Am. Chem. Soc.*, 1907, xxix., 1695) on the behaviour of stannic iodide in solution in liquid ammonia are especially illuminating in this connection. When a limited quantity of liquid ammonia is brought into contact with stannic iodide to which a minute quantity of ammonium iodide has been added, the tin salt dissolves to form a dense colourless and clear solution. When additional ammonia is distilled into the tube in such a manner as not to mix its contents, the separation of a white precipitate is observed, occupying a zone between the concentrated solution of the stannic iodide and the freshly distilled ammonia. On shaking the tube and thus mixing its contents the precipitate disappears. On again distilling ammonia into the tube, the precipitate reappears, to disappear again on shaking the tube. The separation of the precipitate may be observed several times by repeating the operations thus described. After a relatively large amount of liquid ammonia had been added, the precipitate becomes permanent, and the separation of tin from the solution is complete, as is shown by the observation that the addition of potassium amide to the supernatant solution fails to produce any further precipitation. The addition of any considerable quantity of ammonium iodide to the solution in the beginning prevents the ammonolysis of the salt. Whether in this particular instance the product of ammonolysis is an ammonobasic salt, or an amide, imide, or nitride of tin, free from iodine, has not been determined. The remarkably close parallelism between the phenomena just described and the familiar action of water on acid solutions of antimony chloride and bismuth chloride is so obvious as to require no further comment.

The ammonobasic salts of definite composition which have so far been obtained are the ammonobasic mercuric halides of the respective formulæ $NH_2-Hg-Cl$, $Hg:N-Hg-Br$, and $Hg:N-Hg-I$, and the ammonobasic lead iodide of the formula $Pb:N-Pb-I.2NH_3$. The reactions whereby these compounds have been obtained are represented by the equations—

$$HgCl_2+2NH_3=NH_2-Hg-Cl+NH_4Cl,$$
$$2HgBr_2+4NH_3=Hg:N-Hg-Br+3NH_4Br,$$
$$2HgI_2+4NH_3=Hg:N-Hg.I+3NH_4I,$$
$$2PbI_2+6NH_3=Pb:N-Pb-I.2NH_3+3NH_4I,$$

the amount of ammonobasic salt formed being increased to a reasonable yield, when desired, by the addition of limited quantities of potassium amide.

The ammonobasic salts which have thus been obtained as definite chemical compounds, as well as the others described above as having been observed qualitatively, all appear as insoluble amorphous precipitates (Note 13), characteristics which, as is well known, attach to the more familiar aquobasic salts. Even the tendency of the latter class of products to form basic mixtures of more or less indefinite composition is exemplified in the failure of

attempts (Franklin, *Journ. Am. Chem. Soc.*, 1905, xxvii., 849) to obtain ammonobasic compounds of definite composition from either aluminium of antimony iodide. In the case of antimony iodide it is interesting to note that continued agitation, through several weeks, of the finely divided salt with liquid ammonia—which, as the ammonia abstracted iodine from the salt in the form of ammonium iodide, was from time to time replaced by fresh solvent—failed, in the hands of Fitzgerald, to yield a compound of definite composition.

In addition to the compounds of mercury, two other representatives of the class of ammonobasic salts are found described in the literature. The ammonobasic titanium halides represented by the formulæ $N{\equiv}Ti{-}Cl$ and $N{\equiv}Ti{-}Br$ have been prepared by Ruff and Eisner (*Ber.*, 1908, xli., 2250) by the action of liquid ammonia on the chloride and bromide of titanium respectively.

11. *Ammonobasic Mercuric Salts.*—The formation of the ammonobasic mercuric salts $NH_2{-}Hg{-}Cl$, $Hg{:}N{-}Hg{-}Br$, and $Hg{:}N{-}Hg{-}I$ by the ammonolysis of mercuric chloride, bromide, and iodide respectively in liquid ammonia solution are facts which have an important bearing upon the question of the constitution of the large group of the so-called mercuriammonium compounds, a question which has never received a satisfactory answer.

Since these ammonobasic mercuric salts, the preparation and description of which have been given in a previous paper (*Journ. Am. Chem. Soc.*, 1905, xxvii., 838), cannot be distinguished from the respective products of the action of aqua ammonia on the mercuric halides, it follows that the latter compounds are identical with the former. It is therefore altogether wrong to formulate the ammonobasic mercuric chloride, $NH_2{-}Hg{-}Cl$, as a double salt of dimercuriammonium chloride and ammonium chloride, $Hg_2N^v{-}Cl.NH_4Cl$, and the ammonobasic iodide, $Hg{:}N{-}Hg{-}I$, as dimercuriammonium iodide, $Hg_2N^v{-}I$, as is done in the majority of the dictionaries and handbooks of chemistry.

In a subsequent paper the attempt will be made to show that all the mercury ammonia compounds described in the literature, instead of being ammonium salts in which ammonium hydrogen is substituted by mercury—as the various mercuriammonium theories assume them to be—are, as a matter of fact, either normal mercuric salts with ammonia of crystallisation, or basic products resulting from ammonolysis, or both ammonolysis and hydrolysis, of the normal mercuric salts.

Conclusion.

It has been shown in this paper that an ammonia system of acids, bases, and salts may be formulated on the basis of ammonia as the typical substance, and in a manner entirely analogous to the formulation of the ordinary oxygen acids, bases, and salts as derivatives of water. In other words, a system of acids, bases, and salts has been developed in which nitrogen occupies a position similar to that occupied by oxygen in the system of Lavoisier.

The acids of the ammonia system are the acid amides and imides, including the amides and imides of the non-metallic elements; the bases of the system are the metallic amides and imides; the salts are the metallic derivatives of the acid amides and imides.

In order to emphasise their relations to ammonia, and for convenience in discussing the reactions between representatives of the ammonia system, these acids, bases, and salts are referred to as ammono acids, ammono bases, and ammono salts respectively.

Reactions in liquid ammonia solutions which are strictly analogous to the familiar hydrolytic reactions in water solutions have been discovered and are accordingly designated as ammonolytic reactions. Products which have been named ammonobasic salts are shown to result from the ammonolysis of certain salts of the heavy metals.

It is shown in this paper that the relationships indicated by this system of nomenclature are by no means purely formal. The ammono acids exhibit certain truly acid properties, the ammono bases react in liquid ammonia solutions in a manner strictly analogous to the familiar reactions of the ordinary bases in aqueous solutions, and the ammono salts are as certainly salt-like compounds as are the products of the interaction of ordinary acids and bases.

A considerable number of new representatives of the ammonia system of acids, bases, and salts have been made by means of reactions carried on in liquid ammonia solutions, and are found described in the above pages.

Notes.

10. Howe, *Journ. Am. Chem. Soc.*, 1909, xxxi., 259, first called attention to the remarkable analogies between these aquostannates and ammonostannates.

11. Prepared in the laboratory of Stanford University by G. S. Bohart. Results not yet published.

12. It is interesting to note in this connection that cadmium hydroxide has not been observed to possess amphoteric properties.

13. In two tubes containing mercuric chloride and liquid ammonia which were sealed up six or eight years ago, the white, apparently amorphous precipitates of NH_2HgCl which separated at that time have changed into aggregates of well developed crystals.

THE SCIENTIFIC WEEK.

(From Our Own Paris Correspondent).

A Mercury-bath Level.

Up till now it has generally been necessary to employ a spirit-level for transportable instruments. The best level is that which is formed by the reflexion in a bath of mercury, but the extreme mobility of the surface of this bath has limited its employment to observatory instruments. Only in the prismatic astrolabe has the difficulty been got over by the use of baths of amalgam, but this has also very serious disadvantages. Messrs. André Broca and Florian have managed to contrive an apparatus that has been realised by the Lacour Duthiot establishments where the useful properties of the mercury-bath have been kept, while the production of waves on the surface has been suppressed by trepidations. This result is obtained by placing the mercury-bath in a box completely closed, and by surmounting it with glycerin. The upper part of the box, that is to say the top, is an objective in contact with the glycerin. With these elements an auto-collimative lunette is constituted, and it is possible with a focal distance of 18 c. and an objective with an opening of 28 mm. to regulate the horizontality to about a fraction of a second. The apparatus also does not take up much space, as the lateral walls of the mercury-box have been formed by a spherical zone in which the mercury is raised till on the level at which the tangent plane makes, with the horizon, an angle equal to the angle of the meeting point of the mercury with the top of the box; this suppresses the perturbations of the surface caused by the meniscus, and thus the bath may have a diameter very slightly superior to that of the objective. This apparatus may be used as a seismograph, and if it is made of sufficiently large dimensions, it may also be possible to study with it the perturbations of the vertical.

Volcanic Gases.

In a notice analysed by M. Lacroix, Professor at the Natural History Museum, Messrs. Day and Shephers conclude from experiments made at Mount Kilanea, that amongst the volatile products emanating from lava in fusion, at a temperature of about 1100°, there is to be found an abundance of water-vapour, which has been condensed and studied. This is a confirmation of the observations

made in 1865 at Etna by Fouqué and Silvester. If other observers, as Messrs. Brun and Green, have concluded from other observations made at Kilanea, that the exhalation is dry, it is because they have operated, not on the gases emanating from the lava in a state of fusion, but upon the gases collected near the edge of the crater. In this region of the volcano there is, indeed, a large amount of dehydrated gases and finely-divided sulphur. Prof. Armand Gautier confirmed the observations of his colleague.

The rôle of Heredity in Dogs.

M. Philippe de Vilmorin has undertaken some very curious experiments on the transmission of hereditary characteristics in dogs. M. Edmond Perrier, Director of the Paris Natural History Museum, has notified these experiments to the Academy of Sciences. There are several races of dogs that have no caudal appendage. Thus, the race of Bourbon brach dogs, the Auvergne brachs, the German brachs, the Spanish bretons, the Hungarian shepherd dogs, the long-haired loulous of the Scheldt boatmen have no tails. But is the characteristic hereditary? M. Philippe de Vilmorin has observed about a hundred individuals, and has made about twenty-seven crosses between dogs of different species. According as the dogs have or have not any caudal appendage, and according to the greater or less length of the same, M. de Vilmorin classes them in three categories. The terminology that is employed for the classification of the mollusca has served him for the designation of the canine categories. The Anoura dogs are characterised by the total absence of any tail. The Brachyura dogs have a short tail. The Macroura dogs have, on the contrary, a normal tail. Observation has shown that the character of having no tail dominates according to the law of Mendel. It would then seem that all dogs totally tailless are hybrids. On the contrary, the dogs that have a long tail are of a pure type. By crossing Anoura dogs with Macroura dogs half hybrids and half normal dogs have been obtained. By crossing, on the contrary, Anoura dogs amongst themselves, the dogs obtained without a tail were in the proportion of 75 per cent, and the dogs with a tail in the proportion of 25 per cent. These researches confirm once more the discovery made by Mendel about 1868, which discovery has lain dormant for so many long years. The glory of Mendel is quite recent. It was only forty years after the publication of his first studies concerning the transmission of hereditary characters that the Dutch botanist, Van Vries, in 1900, discovered the laws of Mendel. Mendel was a monk in a Moravian convent near Brünn. He was passionately fond of cultivating his garden, where he hybridised sweet-peas. It was in this way that he discovered the laws of hybridation. Published in a little local review, the *Bulletin de la Réunion Scientifique de Brünn*, these laws remained for a long time hidden. Since Van Vries rescued them from oblivion naturalists and scientists are continually exploring this marvellously rich way which has given many interesting indications concerning the mysterious and complex problems of heredity.

Natural Incubation and Artificial Incubation.

The comparative study of natural incubation and artificial incubation is somewhat difficult, as it can only be made during the season in which it is convenient to procure hatching hens. For this reason the experiments that M. Brechemin has made on this subject were effected during the months of March, April, and May; they concerned, on the one hand, three turkeys, three hens, who were each time charged with a hundred eggs; on the other hand, there was an artificial incubator with a reservoir of water kept hot by means of a little lamp. In this apparatus a hundred eggs were placed each month; naturally the eggs had previously been thoroughly looked through. The results were the following:—Natural incubation—242 fecundated eggs gave 158 chickens; artificial incubation—243 fecundated eggs gave 209 chickens. The experiments were continued by the comparison of artificial breeding and natural breeding, the food being the same for all the chicks. Those given over to the care of the hens and turkeys disposed of a surface of 4000 square metres of free air, whilst the artificial breeder was surrounded by only 600 square metres of ground situated in a place the front part of which was covered with glass. Three months after the eggs were hatched it was seen that there were only 75 chicks left out of the 158 brought up naturally, whereas there were still 194 out of the 209 brought up artificially; that is to say, a loss of more than 50 per cent out of the natural breeding and only 10 per cent out of the artificial breeding. All the same, it must be noticed that the loss is not so great for the natural breeding when the hens are kept in breeding boxes or in closed hen-houses. As a conclusion to be drawn from his trials, M. Brechemin considers that natural hatching and breeding can be indicated for small enterprises and for reproductive breeding broods because they give more vigorous subjects; artificial incubation and breeding must nevertheless be preferred for all breeding enterprises of any extent.

The Evolution of Sea fishing.

Several deep-water fish, of which the zoological museums possess but very few examples, have made their appearance on the Paris fish market. Large quantities of these fish are to be found in the Central Market during the winter months. According to M. Edmond Perrier, Director of the Natural History Museum, these curious facts are the consequence of the evolution of sea-fishing. The fishers now go further and deeper to seek for the fish that are rarely to be found near the coast. For some years past trawlers have been going to fish on the coasts of Portugal, and their nets descend to a depth of 200 metres. Dr. Jugeat, sanitary veterinary surgeon at the Central Market, has noticed many fish like the beryx, of a bright scarlet colour; the *brama*, the *zeides*, the *Dentus marocanus*, the ancient bramides, whose eyes are particularly developed on account of the weak light that penetrates into marine waters at a depth of 200 metres. Very few Parisians consider that they are often given fish to eat that up till now were considered as zoological curiosities.

A Year without any Spots on the Sun.

During the first two quarters of the year 1913 the brilliant surface of the sun remained completely free of spots. M. Guillaume, astronomer at the Observatory of Saint-Genis Laval, near Lyons, has continued his observations during the third quarter. M. Bailland, Director of the Observatory, in a communication in M. Guillaume's name, remarks that also during this period there have been hardly any spots; on the contrary, brilliant faculæ have been observed. Another astronomer of the Lyons Observatory, M. Hajolet, has remarked a certain increase in the stronger magnetic perturbations, which are the only ones that it is possible to observe. The year 1913 is remarkable on account of the absence of spots on the sun. Such a minimum has not been observed since 1810.

Is it Land or a New Island?

General Scholaksky, delegate from the Russian Government to the Conference on the Map of the World, has presented two communications—one concerning a new map, in relief, of Siberia; the other concerning an important discovery that has been made by the hydrographic officers of the Russian Navy instructed with the exploration of the Northern Siberian coast from Behring's Straits to the Tamur peninsula. These officers have discovered a new land, or a new long and narrow island, which extends towards the east as far as the longitude 97° twelve minutes of the Greenwich meridian. It is not yet known how far this land stretches towards the west. The latitude of it is 80° four minutes. It occupies about the same position as Spitzbergen and Franz-Josef's land. The mission has not yet returned from Kamschatka. This news has been transmitted by telegram.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, November 6th, 1913.

Prof. W. H. Perkin, LL.D., F.R.S., President, in the Chair.

The President referred to the heavy loss the Society had sustained through death, during the vacation, of the following Fellows:—E. L. Barret, Paris; J. C. Bell, Manchester; A. Cantin, Mauritius; T. Crossman, Starbeck; J. Davidson, Holywell Green; L. M. Deane, Ilkley; Sir W. N. Hartley, Dublin; J. Lewkowitsch, W. Hampstead; H. Marshall, Dundee; L. Patchett, Batley; M. G. Roy, Chintadrepettah; A. Wallace, Agra.

The following announcement was made:—That, in future, a list of the papers to be read at each Ordinary Scientific Meeting will be advertised in the *Morning Post* on the Wednesday previous to the day of meeting.

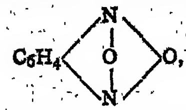
Messrs. C. K. Tinkler and E. Cahen were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Richard Watson Askew, B.A., Brierley, Chelmsford Road, Durban, Natal, South Africa; Sankar Rao B. Badami, M.A., Badami House, Hulsurpet, Bangalore, India; Stanley Charles Bate, B.Sc., 50, Alexandra Road, Upper Norwood, S.E.; Charles Maurice Berlein, B.A., Cross Oak, Berkhamsted; Arthur Bicknell, B.Sc., Balliol College, Oxford; Augustus Pearce Llewellyn Blaster, B.A., Chidham, Potters Bar, Middlesex; Adhor Krishna Bose, 90, Musjeed Baree Street, Calcutta, India; Arthur Bramley, B.Sc., 19, Cambridge Road, Barnes, S.W.; Arthur Joseph Brearley, B.A., 13, Victoria Terrace, Exeter; Bertram Campbell, B.Sc., Beechover, Manor Avenue, Grimsby; Frederick George Carter, Amritsar Distillery, Amritsar, Punjab, India; Santi Pada Chowdry, Economic Research Laboratory, Rewa State Industries, Umaria, India; Francis William Clark, 35, Wilmington Square, W.C.; Herbert Stoddard Coleman, 14, Dunsford Road, Bearwood Road, Smethwick; Thomas James Drakeley, B.Sc., 36, Mitchell Street, Newtown, Wigan; Cyril Duncan Fuller, 62, Hill Street, Totterdown, Bristol; Charles John Dickenson Gair, 39, Cranston Road, Forest Hill, S.E.; Stanton Gibson, B.Sc., 28, Lordship Park, N.; Richard Hargreaves, B.A., Chatburn, Clitheroe; George Alfred Hebden, 78, Norborough Road, Tinsley, Sheffield; Richard Pendarves Hodges, 42, Olive Road, Cricklewood, N.W.; William Francis Hollely, 67, Ross Road, Wallington, Surrey; Alexander Hynd, M.A., B.Sc., 196, Baldridgeburn, Dunfermline; William Johnson, B.Sc., Walton, Stoneygate Avenue, Leicester; Harold Bramfield Jones, Broadway House, Northolme Road, Highbury, N.; Gholam Rasal Khan, B.Sc., Lyallpur, Punjab, India; Sidney Oliver Leivesley, care of W. Leivesley, Esq., Chillagoe, N. Queensland, Australia; William John Lewis, 10, Lightoaks Road, Pendleton, Manchester; Percival James Lycett, Castle Hill, Wolverley, Kidderminster; Frank Clifford Marchant, St. Kilda's, Manor Road, Forest Hill, S.E.; Kunerji Gosai Naik, M.A., B.Sc., Krishnath College, Berhampore, Dist. Murshidabad, Bengal, India; John Allen Nichols, Stanley Mount, New Mills, Stockport; John Thomas Pattison, 72, Bath Road, Southsea, B.O., Portsmouth; Wilfrid Roberts Powell, B.A., 14, Marlborough Road, Richmond, Surrey; Henry Edward Findlater Pracy, 25, Grosvenor Park, Camberwell, S.E.; John McArthur Stuart, Balliol College, Oxford; Robert Tennant, 4, Park Terrace, Queen's Park, Glasgow; Henry Walker, 10, Melrose Terrace, West Kensington Park, W.; Henry Wood, The Limes, 62, Culverden Road, Balham, S.W.

Of the following papers, those marked * were read:—

*266. "*The Conversion of Orthonitroamines into isoOxadiazole Oxides (Furoxans).*" By Arthur George Green and Frederick Maurice Rowe.

Whilst *o*-nitroaniline on alkaline hypochlorite oxidation is quantitatively converted into benz*iso*oxadiazole oxide,—



and 2 : 4-dinitroaniline (when an alcohol is present) into a chloromethoxy-(or ethoxy)benz*iso*oxadiazole oxide, the presence of an amino-, acetylamino-, azo-, or sulphonic group in the para-position occasions a complete disruption of the benzene ring, and only in the case of the sulphonic acid was a small quantity of a benz*iso*oxadiazol oxide produced.

The two isomeric *o*-dinitrobenzidines (Cain, Coulthard, and Micklethwait, *Trans.*, 1912, ci., 2298), when subjected to hypochlorite oxidation under like conditions, yield entirely different products. Whilst the isomeride melting at 275° (regarded by these authors as 3 : 5′-dinitrobenzidine) produces a typical furoxan,—

$$O_2\equiv{}^{N}_{N}{>}C_6H_3{\cdot}C_6H_3{<}^{N}_{N}\equiv O_2,$$

readily convertible on reduction into a diphenoquinone tetraoxime, $C_6H_3(:NOH)_2{\cdot}C_6H_3(:NOH)_2$, and a bisbenz*iso*oxadiazole,—

the isomeric *o*-dinitrobenzidine melting at 233°, regarded as the 3 : 3′-derivative, gives a reddish brown crystalline compound of the formula $C_{12}H_6O_4N_4$, which is probably an internal azo-compound.

$$\begin{array}{l} C_6H_3(NO_2){\cdot}N \\ \quad | \qquad\quad \| \\ C_6H_3(NO_2){\cdot}N \end{array}$$

The above bisbenz*iso*oxadiazole oxide (bisbenzfuroxan) crystallises from chlorobenzene in pale yellow thin hexagonal plates, melting at 211°. The corresponding bisbenz*iso*oxadiazole (bisbenzfurazan) forms yellow needles, which melt at 244°. The diphenoquinonetetraoxime is a brown amorphous powder, soluble in alkalis. The authors have also repeated and confirmed the results of Drost (*Annalen*, 1899, cccvii., 54) on the nitration products of benz*iso*oxadiazole oxide. Both the mono- and the di-nitrobenz*iso*oxadiazole oxides, which are thus obtained, have strongly marked acid properties, turning Congo paper blue, and dissolving readily in aqueous alkalis.

*267. "*The Constitution of Aniline-black.*" (Part IV.). By Arthur George Green and William Johnson.

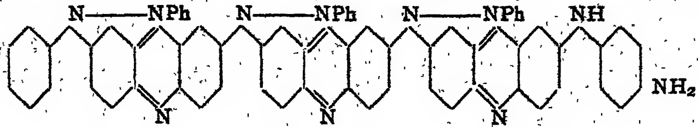
In further support of Green and Wolff's formula (A) for aniline-black base (chlorate oxidation) (*Proc.*, 1912, xxviii., 250) the following data have been obtained:—

1. On oxidation of aniline-black with lead peroxide and sulphuric acid a yield of benzoquinone is obtained, which corresponds with that required on the assumption that all the mono- and di-substituted benzene nuclei, but not the tri-substituted, will yield benzoquinone.

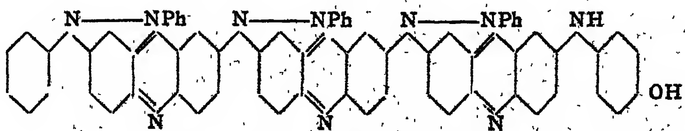
2. In presence of an excess of mineral acid aniline-black absorbs one molecule of sodium nitrite corresponding with the formation of a monodiazonium salt. Hence the terminal nitrogen atom forms an amino- and not an imino-group, and the chain must be an open one.

3. Titrations with hydrochloric acid have shown that aniline-black, in common with emeraldine and nigraniline, yields a non-hydrolysable dihydrochloride and a trihydrochloride, in which one molecule of hydrogen chloride is readily hydrolysed. Two of the nitrogen atoms are therefore strongly basic (quinonoid), whilst a third is weakly basic (amino-group). Leucoemeraldine, which contains no quinonoid nitrogen, does not give a stable hydrochloride.

4. Nigraniline does not condense with secondary aromatic amines, but only with primary amines.



(A).



(B).

5. The variety of aniline-black produced in solution by oxidation with chromic acid and known as "single bath black," or "bichromate black," has given results which indicate that it is the hydroxy analogue of ordinary aniline black (B). It is less basic than ordinary aniline-black, forming a non-hydrolysable dihydrochloride, but not a trihydrochloride. On oxidation it gives a yield of benzoquinone consistent with the formula given. In the above formulæ the colouring-matters are represented as anhydro-bases, but in both cases analysis indicates the presence of $1H_2O$ more, a fact explainable on the assumption that one phenylazonium group is present as an hydroxide or two such groups as an oxide.

DISCUSSION.

Professor J. T. HEWITT agreed with Dr. Lowry in not liking an ortho-quinonoid formula for the free anhydrous bases of the safranine series. The linking of a quinquivalent nitrogen atom to a tervalent nitrogen atom attached to the same nucleus but in the meta-position seemed quite improbable, and when similar structures were given to *apo*safranone and its derivatives, the compounds were represented as betaines of a weakly acid phenolic group with a quaternary ammonium (powerfully basic) compound. This was at variance with the actual properties of *apo*safranone and its hydroxy-derivatives, since their basic properties were feeble. Arguments of a similar character might be urged against Professor Green's quaternary ammonium oxide formula for the hydrates of compounds of aniline-black type.

*268. "*The Constituents of Senna Leaves.*" By FRANK TUTIN.

Three specimens of senna leaves have been submitted to examination, namely—(I.) Tinnevelly senna leaves (*Cassia angustifolia*, Vahl; (II.) senna leaves from Lima, Peru, which were found to be botanically identical with the Tinnevelly leaves; and (III.) Alexandrian senna leaves (*Cassia acutifolia*, Delile).

The Tinnevelly leaves yielded, in addition to a small amount of essential oil, chlorophyll, and resinous products, the following definite substances—(i.) Salicylic acid; (ii.) rhein; (iii.) kæmpferol; (iv.) aloe emodin; (v.) *kaempferin*, $C_{27}H_{30}O_{16},6H_2O$ (m. p. 185—195°), a new glucoside of kaempferol; (vi.) a mixture of the glucosides of rhein and aloe-emodin; (vii.) the magnesium salt of an unidentified organic acid; (viii.) dextrose; (ix.) myricyl alcohol; (x.) a phytosterol; (xi.) a phystosterolin, $C_{33}H_{56}O_6$; (xii.) palmitic and stearic acids.

The Peruvian and Alexandrian senna leaves contained the above-mentioned compounds, with the exception of the magnesium salt, and, in addition, *iso*rhamnetin. The latter also occurred in the form of a glucoside.

The statements of Tschirch and Hiepe (*Arch. Pharm.*, 1900, ccxxxviii., 427), that senna leaves contain "senna-*iso*emodin," "sennachrysophanic acid" (chrysophanol), a "substance, $C_{14}H_{10}O_5$," and sennarhamnetin," cannot be confirmed, it having been ascertained that the anthraquinone derivatives present consist solely of rhein and aloe-emodin, whilst the flavone product is either kaempferol, or a mixture of the latter with *iso*rhamnetin.

*269. "*A Series of Mixtures of Nitro-compounds and Amines, which are Coloured in the Liquid State only.*" By CHARLES KENNETH TINKLER.

Certain nitro-compounds, when dissolved in fused diphenylamine and other amines, give strongly coloured solutions. The colour, however, entirely disappears on complete solidification of the mixture.

The most suitable substances for the demonstration of this phenomenon are mixtures of diphenylamine with one of the following nitro-compounds: *o*-, *m*-, and *p*-chloronitrobenzene, *m*- and *p*-nitrobenzaldehyde, *p*-bromonitrobenzene, tetranitromethane. By enclosing one of these mixtures between two test-tubes placed one inside the other, the phenomenon is well demonstrated. Thus, a mixture of diphenylamine and *p*-chloronitrobenzene, which is colourless at the ordinary temperature, acquires a reddish yellow colour when held in the hand, and loses this colour when the temperature falls.

A mixture of diphenylamine and *p*-nitrobenzaldehyde shows a deep red colour at slightly above body temperature, returning to the colourless state on cooling.

A mixture of diphenylamine (solid) and tetranitromethane shows a dark brown coloration, but in a freezing mixture this colour is entirely removed.

From analogy to compounds of amines and nitro-derivatives, such as trinitrobenzene (Hepp, *Annalen*, 1882, ccxv., 344; Sudborough, *Trans.*, 1901, lxxix., 522; 1902, lxxxi., 587, &c.; Noelting and Sommerhoff, *Ber.*, 1906, xxxix., 76, and others), it is possible that the colour of these mixtures is due to the combination of the nitro-derivative and amine in the liquid state only. No direct evidence of compound formation has, however, so far been obtained from the various physico-chemical investigations which have been carried out.

Certain phenols and other substances may be substituted for the amine in the demonstration of the phenomenon, and the investigation is being extended in this direction.

DISCUSSION.

In reply to the President, Dr. TINKLER said that the transient colorations produced were usually orange-red or red, although in the case of diphenylamine and tetranitromethane a very dark brown coloration was obtained. No transient blue or green colorations had been observed.

With reference to Dr. Senter's suggestion that the colour might be due to the presence of a small quantity of compound, Dr. Tinkler pointed out that, so far, no such indication had been obtained by the physico-chemical investigations which had been carried out with the mixtures. If, however, a compound was formed at all, it did not exist in the solid state, or the mixture would remain coloured on solidification and precipitation from solution.

270. "*A Study of some Organic Derivatives of Tin as regard their Relation to the Corresponding Silicon Compounds.* Part II. *Condensation Products of Dihydroxydibenzylstannane.*" By THOMAS ALFRED SMITH and FREDERIC STANLEY KIPPING.

Organic derivatives of tin of the general formu

$SnR_2(OH)_2$ are unknown, but various oxides, SnR_2O, insoluble in all organic solvents, have been prepared.

The authors have attempted to obtain compounds of the dihydroxy-type in order to ascertain whether they are capable of existence, and, if so, whether they would give rise to open- and closed-chain condensation products analogous to those recently prepared from diphenylsilicanediol (Kipping, *Trans.*, 1912, ci., 2125).

The first product of the hydrolysis of dibenzyldichlorostannane with dilute potassium hydroxide solution seems to be the potassium derivative of the dihydroxy-compound; from the solution of this substance carbonic acid precipitates a solid, which is probably dibenzyldihydroxystannane, $Sn(CH_2Ph)_2(OH)_2$, but this compound is very unstable, and passes into a condensation product, which has probably the constitution $HO{\cdot}Sn(CH_2Ph)_2{\cdot}O{\cdot}Sn(CH_2Ph)_2{\cdot}O{\cdot}Sn(CH_2Ph)_2{\cdot}OH$.

This condensation product, unlike all the oxides, SnR_2O, is readily soluble in various organic solvents; when heated alone or in boiling bromobenzene solution, it passes into an insoluble oxide, which has probably the molecular formula $[Sn(CH_2Ph)_2O]_3$.

It may be concluded that all the insoluble oxides, $[SnR_2O]_x$, are condensation products of the unknown hydroxides; similarly, the ill-defined acids of the composition H_2SnO_3 are probably mixtures of even more complex condensation products of stannic hydroxide.

271. "*6'-Aminoquercetin.*" By Edwin Roy Watson.

A detailed description of work of which a preliminary account has already appeared (*Proc.*, 1911, xxvii., 163).

272. "*Measurement of the Rate of Reaction by the Change of Volume in Solution.*" By Robert Wright.

Although the alteration of volume resulting from chemical change has frequently been used to follow the course of a gaseous reaction—the formation of water vapour from its elements, for example—still it has seldom or never been applied to the case of reacting solutions. Such solution change is, as a rule, undoubtedly small, but even if it only amounts to about 0·2 per cent of the total volume, it gives a conveniet physical method for the determination of reaction velocities.

A few well-known reactions have been investigated in this manner, but in some cases the change of volume is too small to be of service. For example, on heating an aqueous solution of pyrophosphoric acid, in a sealed tube for several hours at 100°, only a very slight change in the density of the solution takes place, and the same negative result is obtained by a similar heating of a solution of potassium cyanide. The hydrolysis of methyl acetate by sodium hydroxide is accompanied by considerable contraction in the reacting solution, but the change is inconveniently rapid, ard the results are also masked by the rise of temperature which occurs.

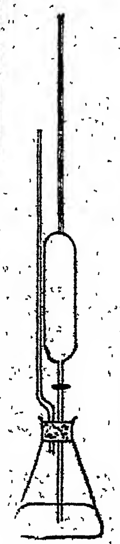
The rate of inversion of sucrose by an acid can readily be followed by means of the change of volume. A mixture of equal volumes of a 20 per cent solution of sucrose with 2N-hydrochloric acid showed the following densities before and after inversion:—

(*a*) After mixing..	1·0474	(*b*) After mixing..	1·0476
After 48 hours	1·0497	After 48 hours	1·0497

thus giving a contraction of volume equal to about 0·2 per cent.

In the determination of the velocity-constant, the apparatus shown was used. A pipette of about 50 cc. capacity has its upper tube of 1 mm. bore and 25 cm. long; the lower tube, which is fitted with a stopcock, passes through a rubber cork, and reaches almost to the bottom of a 150 cc. flask; a side-tube open to the air also passes through the rubber stopper.

The pipette is first charged with a 20 per cent solution of sucrose, which is run into the flask, and a few grains of mercuric iodide are added as preservative; the pipette is then rinsed out and charged with 2N-hydrochloric acid, and the stopcock being closed, it is placed in position in the flask. The apparatus is now immersed in a thermostat at 25°, and allowed to attain the temperature of the bath; the tap is opened, and by applying suction to the side-tube the acid is drawn into the flask; the mixture is well stirred by drawing air through it, and is then forced back into the pipette until it stands at a level of a few cm. from the top of the capillary tube. It is absolutely essential to have some of the mercuric iodide carried into the pipette along with the solution, otherwise fermentation of the sugar will cause minute bubbles of gas to be formed; for the same reason it is necessary to steam out the apparatus before use. The pipette being charged, the tap is closed, and the level of the liquid in the tube read; this gives the zero reading. The fall of the liquid is now read at definite intervals, and a final reading is taken after forty-eight hours, when the total fall should befrom 10 to 20 cm. The velocity constant may now be calculated in a manner quite analogous to that used with the polarimeter.



In the following example a = final distance between the level of the liquid and the top of the tube, and x_1 and x_2 are the distances corresponding with the times t_1 and t_2. Then k, the velocity-constant, is given by:—

$$k = \frac{1}{t_2 - t_1} \log \frac{a - x_1}{a - x_2}.$$

Time in hrs.	Time in mins.	Reading from top. Mm.	K.
0	0	15·0	
0	15	23·0	0·01177
0	30	29·5	0·00483
0	45	35·5	0·00479
1	0	41·3	0·00498
1	30	51·5	0·00489
2	0	60·0	0·00470
2	30	67·0	0·00459
3	0	73·5	0·00473
48	0	a = 116·0	

Leaving out of consideration the first value of K which is affected by the rise of temperature at the beginning of the reaction, it is seen that the numbers agree to within about 5 per cent of each other, the true value given by the polarimeter being 0·00470.

(We are indebted to the Chemical Society for permission to reproduce the accompanying woodcut).

273. "*Amalgams containing Silver and Tin.*" By William Arthur Knight and Reginald Arthur Joyner.

It was again shown that the ageing of alloys of silver and tin is not due to superficial oxidation. A bar of alloy does not age appreciably even after fifteen days at 115°, whereas filings of the same bar are aged after half-an-hour at 100°. Hence it is concluded that ageing is not due to any uncatalysed polymorphic change in the Ag_3Sn contained in the alloy. It was also proved that ageing is not due to sorption of oxygen by the filings. A further hypothesis to be tested is that it may be due to catalytic action of the iron or products of iron introduced during the filing.

The equilibrium of the metals silver, tin, and mercury at temperatures of 63°, 90°, 166°, and 214° has also been studied. The liquidus has been completely determined at these temperatures, and consists of a line roughly parallel to the Sn-Hg side of the equilateral triangle. At 63° this line only extends about one tenth of the distance across the diagram, whereas at 214° it stretches nearly the whole way across. The solidus has not, as yet, been determined

accurately, but there are good reasons for considering that, commencing at the point Ag_3Hg_4, it extends across the diagram roughly in the direction of Ag_3Sn. It has been proved that the substances represented by points on the solidus must be solid solutions.

(To be continued).

NOTICES OF BOOKS.

Chemical Technology and Analysis of Oils, Fats, and Waxes. By Dr. J. LEWKOWITSCH, M.A., F.I.C. Fifth Edition. Volume I. London: Macmillan and Co., Ltd. 1913.

SOME new analytical methods are described in the fifth edition of this treatise, and a considerable amount of new material has been added to it, so that its bulk has had to be much increased. The first volume deals with the chemistry and analysis of the oils, fats, and waxes. In the early chapters the classification and the physical and chemical properties are discussed, and the saponification of fats and waxes and the chemical nature of their constituents. Physical and chemical methods of examining them are also described, quantitative preceding qualitative methods, and the examination of fixed fatty acids and of unsaponifiable matter is treated in the last chapters. The second and third volumes are promised quite shortly, and with them the complete index will be issued.

Digitalis Assay. By W. HARRISON MARTINDALE, Ph.D. (Marburg), F.C.S. London: H. K. Lewis. 1913.

THE colorimetric method of assaying digitalis described by the author of this book has the advantages of being easy to perform and requiring only simple apparatus. The whole operation takes about three hours, and when carried out by an investigator of average skill it is claimed that, although it cannot be relied upon for absolute accuracy it will show, without leaving any room for doubt, whether a given specimen is exceptionally weak or strong. The author strongly deprecates the use of animals for the routine work of testing, and contends that for all ordinary purposes his method is as valuable as the physiological method. The book contains short abstracts of most of the work that has been published on digitalis assaying, and besides describing in full detail the perfected method of carrying out his test the author gives some account of the preliminary experiments from which it was evolved. He has also something to say about the importance of the standardisation of the drug and about the ideal conditions for the growth of the plant. From the results of his work he has formed the opinion that any method of standardisation based upon the content of Digitoxin cannot be regarded as really satisfactory, since the water-soluble constituents are not entirely without therapeutic action, and digitoxin itself appears to be not quite insoluble in water.

A Text Book of Quantitative Chemical Analysis. By ALEXANDER CHARLES CUMMING, D.Sc. and SYDNEY ALEXANDER KAY, D.Sc. London: Gurney and Jackson. 1913.

THIS book on quantitative analysis will provide the student with a good training in the subject, and in consequence of its comparatively wide scope it will be found specially suitable for the use of those who cannot give very much time to practical chemistry, and who nevertheless require a good general knowledge of all the most important branches of analytical work. It begins with volumetric analysis, which in the author's opinion has more educative value than gravimetric work. Electrolytic methods are ncluded and some colorimetric estimations, as well as gas analysis and easy organic combustions. The treatmen of some fairly simple alloys and ores is discussed, and a good feature is the prefacing of each detailed description by a short outline of the method to be employed, so that the student is given no excuse for not knowing exactly what he is driving at. In one section of the book the systematic quantitative analysis of all the common metals and radicles, arranged alphabetically, is given, including both separations and determinations, and this section will be very useful for reference and revision.

Pyrites in Canada. By ALFRED W. G. WILSON, Ph.D Ottawa: Government Printing Bureau. 1912.

THE extension of the manufacturing industries in Canada, and in particular of the sulphite pulp process, has led to many enquiries as to the country's supplies of pyrites, for which there is a large and growing demand. The writer of this bulletin has endeavoured to bring together all that is known about the occurrence, dressing, and uses of pyrites in Canada, and gives practical information for the benefit of both the producer and the consumer. Details of the localities in which the ore has been found are included, and accounts are given of methods of working and of the different types of furnaces used in roasting it. The manufacture and uses of sulphuric acid are also described, and a chapter on the Paper Manufacturing Industry deals with the use of pyrites as a substitute for sulphur in the sulphite fibre industry.

The Flash Point of Oils. By IRVING C. ALLEN and A. S. CROSSFIELD. Washington: Government Printing Office. 1913.

THIS Technical Paper, issued by the Bureau of Mines, contains short descriptions of different types of instruments for determining the flash point of oils, and also a complete bibliography of methods and apparatus. The authors discuss at length the various factors which have to be taken into consideration in the determination, and recommend as the most reliable instruments the Abel-Pensky and the Pensky-Martens testers. The construction and manipulation of both of these are described in some detail, and the use of simple testers, which can be employed when great accuracy is not required, is also shortly treated.

Our Artesian Waters. By R. S. SYMMONDS. Sydney: W. A. Gullick. 1912.

THE author of this bulletin on the Artesian water supply of Australia believes that the diminution in the flow and pressure of certain bores is due not to lack of water, but to leakage and the corrosion of casings, and in the bulletin he brings forward the evidence upon which he bases this important conclusion. He also discusses the analysis of the waters from different localities and the injurious effects of the alkaline salts in them. Some very interesting culture experiments are described, and the striking results which have been obtained by treating the soil with dilute nitric acid to neutralise the alkalinity are illustrated.

The Scientists' Reference Book and Diary for 1914. Manchester: James Woolley, Sons, and Co., Ltd.

THIS is a very convenient sized pocket-book, well bound in morroco leather, with a good plain diary for the year. There is ample space for memoranda, &c., card and postage stamp pockets, together with a reference book of 132 pages, printed on thin paper containing the usual budget of information that is continually needed by the professional man (or woman). A very compact review of "Science in 1913," by E. S. Grew, M.A., is included, in which the various advances that have been made during the year are briefly noted.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances des l'Académie des Sciences. Vol. clvii., No. 18, November 3, 1913.

Alkylation of β- and γ-Methylcyclohexanones by means of Sodamide.—A. Haller.—When the β- and γ-methylcyclohexanones are subjected to methylation or ethylation by means of a halogen compound in presence of sodamide, the ketone always condenses with itself besides undergoing the desired alkylation. The condensation is more marked the further the methyl group is from the ketonic group; it attains its maximum with cyclohexanone, the non-methylated ketone. Other things being equal the condensations of the ketones with themselves are more marked in ethylation than in methylation. The yield of alkylated ketone is greater the nearer the original methyl is to the ketone group.

Distillation of Oil under Reduced Pressure.—Amé Pictet and Maurice Bouvier.—The authors have distilled a fatty oil from Montrambert (Loire) under a reduced pressure at as low a temperature as possible, and have investigated the products, which separate into two layers; an aqueous solution (about 1·5 per cent by weight of the oil) possessing an acid reaction, and not containing ammonia, and a special tar (about 4 per cent). This tar, which the authors call "vacuum tar," differs essentially from ordinary tar in properties and composition. It is fairly fluid, light brown in colour, and lighter than water. It contains very little aromatic substance or none at all, and all its properties resemble those of petroleum, especially Caucasian petroleum. When it is subjected to a second distillation the principal constituents of ordinary tar are obtained, and hence "vacuum tar" is an intermediate product of the distillation of oil at the ordinary pressure, and at a higher temperature it undergoes decomposition into the products which constitute ordinary tar.

6-Aminopiperonal.—Aug. Rilliet and L. Kreitmann.—6-Aminopiperonal can be prepared by the reduction of 6-nitropiperonal by means of sodium sulphide, but it is necessary to use an indirect method by which the aldehyde group is protected against a secondary action of the sulphide and also against a condensation with the amine group formed. For this purpose 6-nitropiperonal is condensed with paratoluidine, and the aminopiperonylideneparatoluidine obtained is reduced with sodium sulphide and then hydrolysed by boiling with water made slightly alkaline.

Atti della Reale Accademia dei Lincei. Vol. xxii. [ii.], No. 5, 1913.

Decomposition of Racemic Amino Acids by means of Active Acids.—Amedeo Colombano and Giuseppe Sanna.—The authors have endeavoured to split up glycocoll and α-alanine into their optical isomers by means of *d*-camphosulphonic acid and *d*-bromocamphosulphonic acids. In both cases the attempts always failed, although the experimental conditions were varied within wide limits.

Vol. xxii. [ii.], No. 6, 1913.

Decomposition of α-Alanine into its Optical Antipodes by means of Active Acids.—Amedeo Colombano and Ginseppe Sanna.—α-Alanine can be split up into its optical antipodes by means of such active acids as campho or bromocampho-sulphonic acids, if it is first esterified by Fischer's method. The esters are substances which are readily characterised by their boiling-points, solubility, and melting-point of their picrates.

MISCELLANEOUS.

Anglo-American Exposition, London (May—October), 1914.—The Committee of the Chemical Industries Section of the Anglo-American Exposition of 1914 is hoping to arrange the most extensive collection of exhibits ever brought together and to make it worthy of the British Empire, and undoubtedly the exhibits from the United States will be of the highest order. The Exposition will give manufacturers an unique opportunity of bringing British chemical industries to the notice of visitors from all parts of the world. A very influential committee has been appointed, and the following are the sub-sections in which the exhibits will be arranged:—*Sub-section* I.—Apparatus and Machinery common to Chemical Industries. *Sub-section* II.—Mineral Acids, Alkalis, and all kinds of Salts. *Sub-section* III.—Materials and Processes connected with Heating and Lighting. *Sub-section* IV.—Explosives of all kinds and Matches. *Sub-section* V.—Sugar, Starch, and Alcoholic Products. *Sub-section* VI.—Appliances and Processes for the Treatment of Sewage, &c. *Sub-section* VII. Dyes, Pigments, &c. *Sub-section* VIII.—Paper and Artificial Textile Materials. *Sub-section* IX.—Leather, Rubber, &c. *Sub-section* X.—Drugs and Pharmaceutical Products, &c. *Sub-section* XI.—Essential Oils and Perfumes. *Sub-section* XII. Tobacco and Snuff.

The National Physical Laboratory. British Radium Standard.—By resolution of the International Standards Committee in March, 1912, a preparation of 21·99 mgrms. of pure radium chloride, prepared by Mdme. Curie, was declared to be the International Standard, and deposited at the Bureau International des Poids et Mesures at Sèvres. The National Physical Laboratory, Teddington, Middlesex, is in possession of the British Radium Standard, which has been certified by the International Committee after comparison with the International Standard. The Laboratory is prepared to undertake the standardisation of radium and mesothorium preparations by comparison with the Standard. For the present the Laboratory will confine itself to the testing of specimens which permit the use of methods depending on the measurement of the penetrating γ-rays. This method requires that the preparation shall have been completely closed in a containing vessel for at least six weeks before the test, as until that time has elapsed the intensity of the γ-rays is not proportional to the quantity of radium present. If the specimen, after a test lasting ten days or more, proves to be in radio-active equilibrium a certificate will be granted by the Laboratory, giving the date of test and the equivalent content of metallic radium within the limits of accuracy of the measurement, provided this content is in excess of 1 mgrm. It is requested that when possible the specimen shall be enclosed in a thin-walled vessel of small dimensions. The scale of fees is as follows:—Samples up to and including 10 mgrms. metallic radium, £3 3s.; more than 10 mgrms. and up to and including 40 mgrms., £4 14s. 6d.; more than 40 mgrms. and up to and including 80 mgrms., £7 7s. In the case of a sample containing less than 1 mgrm. of metallic radium a certificate will not ordinarily be issued; its place will be taken by a statement to the effect that the sample does not contain more than some specified amount of the metal. A person wishing to send radium for test must advise the Laboratory of his intention at least one day previous to sending the specimen. The letter of advice should state approximately the value of the specimen and the method by which it is being sent. All communications and specimens should be addressed to The Director, The National Physical Laboratory, Teddington, Middlesex, and all packages containing specimens should be clearly marked "R Department."

MEETINGS FOR THE WEEK.

TUESDAY, Dec. 30th.
THURSDAY, Jan. 1st.
SATURDAY, „ 3rd. } Royal Institution, 3. (Christmas Lectures, adapted to a juvenile auditory). "A Voyage in Space," by Prof. H. H. Turner, D.Sc., F.R.S.

INDEX.

END OF VOLUME CVIII.

THE

CHEMICAL NEWS

AND

JOURNAL OF PHYSICAL SCIENCE.

WITH WHICH IS INCORPORATED THE "CHEMICAL GAZETTE."

A Journal of Practical Chemistry

IN ALL ITS APPLICATIONS TO

PHARMACY, ARTS, AND MANUFACTURES.

EDITED BY

SIR WILLIAM CROOKES, O.M., D.Sc., F.R.S., &c.

VOLUME CIX.—1914.

LONDON:

PUBLISHED AT THE OFFICE, 16, *NEWCASTLE STREET, FARRINGDON ST.,*
E.C.

AND SOLD BY ALL BOOKSELLERS.

MDCCCCXIV.

LONDON:
PRINTED BY EDWIN JOHN DAVEY,
16, NEWCASTLE STREET, FARRINGDON STREET,
E.C.

THE CHEMICAL NEWS.

VOLUME CIX.

EDITED BY SIR WILLIAM CROOKES, O.M., D.Sc., Pres.R.S., &c.

No. 2823.—JANUARY 2, 1914.

REVIEW AND INTERPRETATION OF RECENT EXPERIMENTS WHICH EXTEND AND ELUCIDATE THE DOMAIN OF THE PASSIVITY OF METALS.*

By Dr. D. REICHINSTEIN, Zurich.

1. *Historical.*

FARADAY (Letter to Brayley, July 8, 1836, *Lond. and Edinb. Phil. Mag.*, 1836, ix., 122) ascribes the discovery of the passivity to Keir (*Phil. Trans.*, 1790, pp. 374 and 379), who observed in 1790 that iron was not attacked in strong nitric acid, but assumed a "changed" state.

The problem was, however, investigated only in the thirties of the last century by Faraday and by Schönbein; the latter introduced the term "passivity." The difference of opinion between the two originators of the problem is of high historical interest. Faraday's views as to the nature of passivity were interpreted by Schönbein (*Pogg. Ann.*, xxxvii., 390; xxxviii., 444; xxxix., 342) to the effect as if Faraday saw the cause of the passive behaviour of a metal in the formation of a well-developed oxide on the metallic surface, and Faraday is still frequently being called the originator of the oxide theory of passivity. In my opinion Faraday may with equal right be regarded as the originator both of the oxide theory and of the most modern theories of gas charges and metal-oxygen alloys; and in this sense I regard the theory which I am going to present merely as a logical consequence of the views of Faraday.

In support of this statement I quote the beginning of a letter which Faraday addressed to R. Taylor (*Phil. Mag.*, 1837, x., 175) on January 21, 1837:—

"Dear Sir,—I am much obliged to you for a sight of Mr. Schoenbein's paper, the experiments and observations in which are excellent. The cause of the phænomena he has so well distinguished is indeed exceedingly difficult to be distinguished at present, and I was in hopes that the doubt on my mind when I ventured the view referred to would be evident from my words. My strong impression is," &c. (*Phil. Mag.*, 1836, ix., 61). "Moreover, Mr. Schoenbein and also M. Aib. Mousson, in an attempt which he has made to explain the cause (*Bibliothèque Universelle de Genève*, 1836, p. 165), have not given my view clearly. I have said that my impression is that the surface of the metal is oxidised, or else that the superficial particles of the metal are in such relation to the oxygen of the electrolyte as to be equivalent to an oxidation, meaning by that, not an actual oxidation, but a relation. . . ."

Faraday further alludes to the researches of Nobili on the colours of thin plates, and he expresses the view that the latter went much further still in the opinion that skins of oxygen and acid may lastingly adhere to the surfaces of platinum, iron, and steel without entering into chemical combination with the metal.

The above quoted letter by Faraday to Taylor further contains, near its end, the following words:—"And my opinion of the cause of the phænomena as due to a relation of the superficial particles of the iron to oxygen. . . ."

From these views of Faraday has arisen the oxide theory of passivity which has been advocated up to the most recent days (*e.g.*, by F. Haber and F. Goldschmidt, *Zeit. Elektrochem.*, 1906, xii., 49).

The theory which I am going to develop is further connected with the views of M. Le Blanc (*Zeit. Elektrochem.*, 1900, vi., 476), who first expressed the idea that it is velocity phenomena which condition passivity. This assumption has successfully been developed and specialised by Fredenhagen (*Zeit. Elektrochem.*, xi., 857, and *loc. cit.*), who makes the occurrence of passivity dependent upon "a coherent, uniform gas charge"; finally Muthmann and Fraunberger (*Sitzber. Bayer. Akad. Wissensch. München: Math.-Phys. Kl.*, 1904, 236) have recognised that this gas charge has the character of an alloy.

The question now, which I put to myself, and which is not discussed by any of the actual theories, is how the transition is taking place from the active state of a metal into the passive state. This question is to receive an answer which can quantitatively be tested by calculations.

Before we pass to the discussion of this question, however, we have to acquaint ourselves with a series of experiments of the very latest dates, some of which have extended the domain of passive phenomena, while others are able to introduce us into the labyrinth of passivity.

2. *Chemical Polarisation of Reversible Active Metallic Electrodes.*

Before the year 1910 all the metals were distinguished as active and passive, and if there was a tendency to look for the cause of passivity in slowly progressing chemical reactions, *i.e.*, in a slow rate of ion-formation, people held on the other side that with active metals anodically treated the formation of ions took place with infinite velocity, and that any polarisation observed with active metals had to be designated a concentration polarisation or a diffusion polarisation; that is to say, a polarisation which arose owing to the differences in the concentration of the electrolyte caused by the current flow, whilst

* A Contribution to the General Discussion on "The Passivity of Metals" held before the Faraday Society, November 12, 1913. (Translated from the German.)

diffusion tended to balance this difference in concentration.

I should like to emphasise in this place already that these definitions of chemical or of concentration polarisation are inappropriate, and that they fail in complicated cases. For the occurrence of concentration differences is not characteristic for the diffusion polarisation. With one and the same electrode different polarisations are observed, always as results of different concentrations of the substances in question. The point is rather, which process is opposing the differences in concentrations to which the electric current gives rise, *i.e.*, whether this compensation is of a chemical nature or a diffusion phenomenon. Hence it would, in my opinion, be appropriate to introduce a definition like the following:—If in any observed polarisation the substitution of a real process by an imaginary *chemical* process, proceeding at infinite velocity, would make the polarisation vanish, we should have to deal with a *chemical polarisation;* if a *diffusion* proceeding at infinite rate should have the same effect, we should have to deal with a *diffusion polarisation.*

Now Le Blanc described in 1910 some experiments which have revolutionised our conception of active and passive metals ("Die elektromotorischen Krafte der Polarisation"). Two proofs can be adduced that there is only a quantitative, not a qualitative, difference between active and passive metals, and that there is, in active metals, a possibility not only of a diffusion polarisation, but also of a chemical polarisation.

These are the proofs:—

In 1904 Thatcher observed that when quite small quantities of so called poisons are added to an electrode, at which an electrolytic oxidation is taking place, the anode potential rises considerably, which indicates that slowly progressing chemical reactions are at play. Le Blanc and his assistants now demonstrated that an addition of poisons to the active electrode Cu | $CuSO_4$ called forth the same effect. Thus 1 cc. of a faintly acid solution of brucine sulphate (of 1 per cent.), added to 100 cc. of a solution of 1N—$CuSO_4$+1N—H_2SO_4, raises the cathodic polarisation from 29 to 148, and the anodic from 14 to 40 millivolts. Strychnine raised the cathode polarisation by 115, the anode polarisation by 18 millivolts, &c.

When we further compare the polarisations of two electrodes under conditions, as equal as possible, of temperature, current density, concentration of the ions, &c., and when we consider that the diffusion rates must, under under those equal conditions, be of the same order of magnitude, we are entitled to conclude that large differences in the polarisation values of the two electrodes can only arise owing to the chemical polarisation of that electrode which possesses the higher polarisation value.

Thus the system Hg | 0·1N—$HgNO_3$+1N—HNO_3 | Hg gave, at a current density of 0·09 amp./$cm.^2$, a polarisation of about 6 millivolts, whilst under the same conditions the system Cu | 1N—$CuSO_4$+1N—H_2SO_4 | Cu gave, with electrodes of Cu quenched in methyl alcohol, 30 millivolts, and with Cu electrodes polished with emery 110 millivolts. Still higher polarisations, of the order of 500 millivolts, were obtained with the system—

$$Fe \mid 1N—FeCl_2+1N—HCl \mid Fe.$$

The third proof for the existence of the chemical polarisation of active electrodes was given by Haber and Zawadzki (*Zeit. Physik. Chem.*, 1912, lxxviii., 241) in 1912, in a paper on the polarisation of solid electrolytes. They found that "solid silver salts show, with a silver anode, a polarisation which increases considerably with falling temperature, and which, in the case of silver sulphate, becomes so pronounced at the temperature of solid carbon dioxide, that the silver anode behaves like an anode of platinum or graphite."

A further proof for the existence of the chemical polarisation of active electrodes is afforded by the fact that additions of free sulphuric acid and of its salts to the Cu | $CuSO_4$ electrode much increase the cathodic polarisation (R. Goebel, "Dissertation," Dresden, 1912, researches carried out under F. Foerster; also D. Reichinstein, *Zeit. Elektrochem.*, 1913, xix., 520, and D. Reichinstein and A. Zieren, *Ibid.*, 530). These two accounts do not yet contain the results of all the experiments made. In order to keep the effect of an addition of a neutral salt quantitatively reproducible, the electrolyte should possess a certain minimum of $H^{\cdot}$ ions; for below a certain $H^{\cdot}$ ion concentration the cathodic current intensity-potential curve of the Cu | $CuSO_4$ electrode takes a qualitatively quite different course from the curve found above this minimum. That indicates that it is purely chemical processes which are responsible for the current intensity-potential curve. Since now all the neutral salts as well as the sulphuric acid itself have the same effect, the increased polarisation is evidently due to the fact that the addition diminishes the concentration of the Cu ions in the electrolyte. What kind of a polarisation is this then —a chemical or a diffusion polarisation?

The first-mentioned case must not be confounded with another, in which the electrolyte contains the same small concentration of $Cu^{\cdot\cdot}$ ions, but in which the neutral salt and the noteworthy concentration of undissociated $CuSO_4$ are missing in the electrolyte.

In contrast to this simple case the more complicated case may be discussed as follows:—Imagine an ideal case, in which the Cu electrode has a considerable concentration of the Cu ions (a), the required minimum of $H^{\cdot}$ ions, and a very small (practically none) concentration of undissociated $CuSO_4$ molecules. At a certain current density at which the cathodic polarisation is still *zero*, a large amount of some alkali salt is added to the electrolyte, in order to reduce the concentration of the Cu ions to $\frac{a}{10}$, *e.g.*, and to set up a certain definite polarisation at the same time. Let us further assume the existence of an electrode which, in the presence of the $\frac{a}{10}$ concentration of its ions (without, however, possessing the 0·9a concentration of the undissociated salt) will mark, *ceteris paribus*, the same polarisation as the Cu electrode referred to. The comparison between this hypothetical electrode and the really existing Cu electrode would suggest:—On the one hand (case 1) the polarisation of the Cu electrode would be caused by a slow (*i.e.*, secondary) transition of the ions into the metallic state; it is assumed that while the current is flowing the concentration of the ions is, by vigorous stirring, kept the same at the electrode surface as in the middle of the electrolyte. On the other hand (case 2) the polarisation of the Cu electrode might be caused by the difference in the concentration near the electrode and in the middle of the electrolyte. The comparison between the Cu electrode and the hypothetical electrode now teaches—

The latter case (2) is only possible when the rate at which the spent Cu ions are replenished by the reaction $CuSO_4 \rightarrow Cu^{\cdot\cdot}+SO_4''$ is infinitely small compared with the rate of diffusion of the Cu ions from the middle of the electrolyte to the surface of the electrode.

The following criteria enable us to distinguish between case 1 and case 2:—

If we can find an electrode such that the concentration of its ions be only $a/10$, that it contain no undissociated salt, and that it do not display any polarisation, *ceteris paribus*, then that Cu electrode would belong to case 1.

If we further succeed in constructing an electrode such hat, with an ion concentration of $a/10$, it show *ceteris paribus* the same polarisation as our Cu electrode, *but practically do not, in an electrolyte of the composition 0·1a concentration of its ions + 0·9a concentration of the undis-*

sociated salt, possess any polarisation, that would be our case 2. It should be added that case 1 represents a pure example of chemical polarisation, whilst case 2 may be regarded as chemical polarisation and as diffusion polarisation as well. For, according to the definition formulated above, in case 2 the polarisation would vanish: by substitution of the real rate of dissociation of the $CuSO_4$ by an infinitely rapid rate of dissociation, and also by substitution of the real rate of diffusion of the Cu ions by an infinitely rapid rate of diffusion.

These complicated polarisation phenomena may probably be more easily investigated in practice than it would appear from this deduction; for I consider that the compensation process of case 2 will, in the predominating number of examples, practically be conditioned only by the dissociation of the undissociated salt. We shall thus either have case 1, or have case 2, in which the dissociation of an undissociated salt will represent the compensation process. The further investigation of the Cu electrode, undertaken for the purpose of deciding the question whether the chemical polarisation owes its existence to the dissociation process indicated, or perhaps to the reduction of the Cu ions (slow because of the small concentration of the latter), has suggested a solution of the problem in favour of case 1 (*loc. cit.*). This consideration is of principal importance for electrodes whose electrolytes consist of complex salts, *e.g.*, Ag | $Ag(CN)_2K$ | electrode.

Interesting examples of chemical polarisation, again not due to slow diffusion of the electrolyte, can be observed when the Cu electrode is rubbed with a little mercury. These cases will be explained lower down.

In looking for an example of an electrolysis which would supply a simple analogy to the described cases of chemical polarisation, that is to say, which would render clear how chemical polarisation can occur with an active electrode, without the metallic electrode losing its capacity of *primarily* (see Note) furnishing ions—in looking for such an analogy (which has been found) a whole series of phenomena was recognised as exemplifying negative depolarisation.

(NOTE.—By a primary electrochemical reaction we understand a reaction with which the passage of the current through the boundary electrode-electrolyte is connected, *e.g.*, the charging of a metallic atom with an electron, or the discharge of an ion. Since this reaction proceeds in synchronism with the electric current, it is more rapid than all chemical reactions—practically of infinite velocity. If the anodic formation of Cu ions progressed primarily, undisturbed, that would not cause any chemical polarisation. The fact that chemical polarisation does occur indicates that another primary reaction is proceeding, and that the $Cu^{\cdot\cdot}$ ion formation is secondary).

3. *Negative Depolarisation.*

(Reichenstein, *Zeit. Elektrochem*, 1913, xix. 520).

What is a depolariser? Imagine a circuit, consisting of a source of electric current having a constant e.m.f. independent of the load, and of a polarisation cell, *e.g.*, of two platinum electrodes in clay cells charged with diluted sulphuric acid, these pots themselves immersed in a common beaker also filled with H_2SO_4. We close the circuit after the current intensity has reached its stationary value, and we add to the electrolyte about the cathode a solution of $CuSO_4$. Then a partly new process will set in at the cathode, and the current intensity will rise. Any material capable of producing these two effects simultaneously is usually called a depolariser. The action of the depolariser appears especially clear to us when it is soluble in the solvent which constitutes the electrolyte, and particularly when it does not chemically react with the electrolyte to which it is added, and does not disturb the state of this electrolyte.

Are there now such materials which, when added to the electrolyte, will not chemically react with it, and will diminish the current intensity instead of increasing it? In other words, are there any *negative* depolarisers? The reply to this question must decidedly be in the affirmative. Let the cathode of the described circuit consist, not of Pt, but of a Pd—H_2SO_4 electrode. When the electrode has, from the beginning, a small H_2 concentration, the electrolysis at not too high current densities will proceed in such a way that the whole hydrogen will be occluded by the electrode, and the polarisation will be very small. We have probably to deal with a very rapid chemical compensation process constituted perhaps by the reaction between the Pd atoms and the primarily formed H atoms.

If we now add, during the electrolysis under suitable conditions, a zinc salt to the electrolyte, the polarisation will increase, the current intensity in the circuit diminish, and a new process will set in: zinc is deposited on the cathode (*Zeit. Elektrochem.*, 1910, xvi.).

The surprising feature in this phenomenon is that, of all the possible processes, it is generally the more rapid which takes place. Which means in the case of the zinc addition that that process which occurs more easily will be impeded, namely, the deposition of hydrogen from the electrolyte by the zinc which would be deposited in minimal quantities (not to be determined by weighing), even at open circuit owing to local action. The zinc hence strengthens the chemical inertia of the reaction between the Pd and H atoms, and acts as a depolariser in a negative sense. I should like to point out in this place already that, if we desire to explain the chemical polarisation of a metallic electrode—let it scarcely be recognisable, or, on the other hand, sufficiently marked to lead to a generation of oxygen at the anode (= passivity)—without denying to the metallic atoms the capability of forming primary ions, then the discharge of OH' ions, which with anodic treatment is simultaneous with the process of charging the atoms, may be regarded as the first step of a negatively depolarising reaction. The analogy is patent; we need only build up the mechanism of the chemical polarisation in a correct way.

The behaviour of real alloys on the anode may further be recognised as an example of negative depolarisation. A. Bürger and I (*loc. cit.*) have anodically investigated the alloys Cu—Ag, Cu—Hg, Cd—Hg, and Cd—Ag.

The noble metals, in amounts as small as possible, are alloyed with the surface of the baser metals. All the alloys examined have qualitatively the same property: they raise the polarisation whilst the equilibrium potential remains equal to that of the unalloyed chemically pure electrode. Thus the polarisation of a Cu electrode which has been rubbed with a little mercury rises *ceteris paribus* from 33 to 161 millivolts. The anodic current density-potential curve of the alloys shows under certain conditions a point of inflection. The alloy is decomposed when the electrolysis is prolonged, and the nobler constituent aggregates or drops down from the electrode.

Of special interest for all these alloys is a strange relation between the velocity of formation of the alloy and the degree of polarisation attainable with the resulting alloy. The Cu electrode may simply be amalgamated by holding it horizontally, the surface free from paraffin facing upward, and pouring some mercury on it, finally adding a few drops of concentrated nitric acid. When the electrode is quickly rinsed with distilled water, a bright mercury surface is left; the nitric acid in this operation plays the part of the soldering liquid in the soldering process.

An electrode prepared in this way, however, hardly marks any greater polarisation than the pure unamalgamated Cu electrode.

In order to prepare an electrode which will show the effect described of the amalgamated Cu electrode, every trace of HNO_3 must be avoided, and the greatest care be observed to deal with pure metals. The mercury is rubbed in the dry into the chemically pure copper surface; this is a tedious operation, and the slower the alloy formation the higher will afterwards be the polarisation realised under anodic treatment.

To the phenomena of negative polarisation might perhaps be joined another class of phenomena. In the cathodic polarisation of mixtures of nickel sulphate and zinc sulphate, of the sulphates of nickel and iron, and of zinc and iron, the polarisation rises frequently up to the value of the baser metal, and this latter metal is likewise deposited (A. F. Walter von Escher, "Kathodische Vorgänge bei der Elektrolyse gemischter Lösungen von Zink- und Eisensulfat," Dissertation, Dresden, 1912; a full literature list will be found there; compare also F. Foerster, "General Electrochemical Behaviour of Metals," *Zsit. Elektrochem.*, 1908, xiv., 153). These processes are not pure examples of negative depolarisation, however, because in the absence of the less noble metal the more noble one is deposited quantitatively, *i.e.*, with a current efficiency of 100 per cent; at the same time hydrogen is generated. These cases are worthy of attention when one of the two metals at least in the salt mixture which is being electrolysed belongs to the cathodically passive metals.

To these experiments, which, as we shall see, introduce us into the ante-room of the passivity phenomena, others may be added, which initiate us directly into the secrets of passivity.

4. *Direct Experiments on the Passivation of Metals.*

Surprise has often been expressed at the fact that a metal turning passive does not, at higher current density, show at least that anodic solubility which belongs to it at small current density. Let a passive metal be dissolved anodically at a low current density a to the extent of 50 per cent, and let it liberate oxygen, so that its dissolution takes place at $\frac{a}{2}$ amp./cm.² of metallic surface. When we increase the current intensity tenfold, the dissolution will not proceed at the rate of $5a$ amp./cm.²; it does not even take place at the former rate $\frac{a}{2}$ amp., but at a much smaller rate. How is this to be interpreted chemico-kinetically? Let us assume that a passive metal Me generates primarily oxygen. Two reactions are possible:—

$$1.\ Me + O + 2H^{\cdot} \rightarrow Me^{\cdot\cdot} + H_2O.$$
$$2.\ O + O \rightarrow O_2.$$

The commencement of reaction (2) is designated "passivity." The example teaches us that passivity is not a result of two competing reactions, for both of which the velocity would increase with increasing oxygen concentration, but: *the passivity is caused by two reactions such that the velocity of the one reaction decreases with increasing* O *concentration, whilst the velocity of the second reaction regularly increases with increasing* O *concentration.*

In 1911 I set myself the task to investigate how the rate of increase of the anodic polarisation potential accompanying the flow of continuous current through a $Pt—H_2SO_4$ electrode differs in the two cases when the Pt electrode is free from oxygen and when it has previously been charged with O_2 (Reichinstein, *Zeit. Elektrochem.*, 1911, xvii., 89; 1913, xix., 672). I made the following observations:—A current impulse is imparted to the combination—

$$Pt \mid 28 \text{ per cent } H_2SO_4 \parallel \text{clay cell}—KI—I \mid Pt \quad \longrightarrow$$

in the direction of the arrow. Its anodical amplitude is 0·1 amp./cm.² of the Pt electrode, its duration 0·026 second. After the expiration of this period follows a spontaneous diminution in the electrode charge lasting 0·028 second. The rest of the anodic charge is then destroyed by short-circuiting the cell for 0·025 second. These three processes succeed one another. (The arrangement comprises a rotating commutator which closes the primary circuit, interrupts it, and closes the short-circuit; the latter could be opened and closed at will during an experiment with the aid of a cut-out). In this way it was possible to obtain, on a photographic plate, oscillographs of the time-potential curves at open and at closed short-circuit.

At open short-circuit this time-potential curve rises steadily up to an asymptotic potential value, which is independent of the time. At closed short-circuit the curve marks a point of inflection corresponding to the moment 0·004 second after closing the circuit. This point is well marked on the oscillogram, and the experiment is easily to be reproduced. I have been able to show this with the aid of the oscillographs at different times to several scientists.

This point of inflection can only be interpreted as indicating that we have to deal with a chemical reaction, the velocity of which first increases and then decreases, as the current quantity (i.e., *together with the oxygen concentration*) *is increasing.* During a period which is smaller than 0·004 second the time-potential curve has the distinct tendency of approaching the time ordinate and a stationary value at low potentials. Every approach to a stationary condition now is connected with an increase in the velocity of the compensation process, *i.e.*, of that process in the absence of which the stationary conditions could not be reached. Now we observe a point of inflection within 0·004 second after closing the circuit, when the potential rises; the velocity of the compensation process is beginning to fail.

Thus the curve velocity-oxygen concentration possesses a maximum.

The compensation process consists of the formation of platinum oxides (see below).

During a period which is smaller than 0·004 second, therefore, a $Pt \mid H_2SO_4$ electrode behaves, at a current density of 0·1 amp./cm.², like an inattackable electrode. The amount of Pt oxide which is formed per sq. cm., when the continuous current is not interrupted, is hence of the order of magnitude $0·004 \cdot 0·1/96540 = 4 \cdot 10^{-9}$ grm.-equivalent.

When afterwards the electrode is polarised for some time with the short-circuit closed, the electrode becomes covered with a yellowish layer which consists of Pt oxides. This does not occur when the short-circuit is open. We remember that platinum is dissolved with a high current yield in KCN solutions by alternating currents, but not by continuous currents. A combination, continuous currents superposed on alternating currents, is utilised in the gold industry.

A lucky accident has led us to the direct experimental recognition of the described maximum of the curve, in which the velocity is plotted as a function of the oxygen concentration.

In Russia a large amount of gold is gained by dissolving the ores in aqueous KCN solution in the presence of air as oxidising agent. This process being very slow, there has been no lack of attempts of trying other oxidising agents.

In this connection Andrejew (*Journ. Russ. Phys. Chem. Soc.*, 1907, xxxix., 1637; *Nachricht. Polyt. Inst., Petersburg*, 1908, ix., 447; *Zeit. Elektrochem.*, 1913, xix., 667) and later Michailenko and Meschterjakow (*Journ. Russ. Phys. Chem. Soc.*, 1912, xliv., 567)—on the instigation of Kistiakowsky—determined the rate of solution of gold in KCN in the presence of oxidising agents. They all found that this dissolution takes place in such a manner that the rate first increases and then decreases with the concentration of the oxidising agent. The velocity-concentration curve displays a well-marked maximum.

We may now pass to the exposition of the theories which aim at bringing all the cases of chemical polarisation under one point of view.

(To be continued).

NOTE ON THE DECOMPOSITION OF HYDROXY ACIDS WITH SODA-LIME.

By LEONARD CARPENTER.

If we consider the reaction—

$$R.CO.ONa + NaOH = RH + Na_2CO_3,$$

where R is an alkyl or aromatic radicle, such as methyl, ethyl, or phenyl, it might be imagined that, by heating the salts of hydroxy acids, alcohols might be obtained. For example, taking lactic acid, if its sodium salt be heated with soda-lime, the following reaction might take place:—

$$\begin{array}{l} CH_3 \\ | \\ CHOH \\ | \\ CO.ONa + NaOH \end{array} = \begin{array}{l} CH_3 \\ | \\ CH_2OH \end{array} + Na_2CO_3$$

Ethyl alcohol.

In order to test this, sodium lactate, intimately mixed with soda-lime, was destructively distilled in an iron tube under reduced pressure at a temperature just below redness. A distillate was obtained consisting of two layers, an upper one consisting of a brown oily liquid, having an odour of peppermint, and a lower aqueous one. By saturating the aqueous portion with solid anhydrous potassium carbonate a liquid was separated which turned out to be acetone. The brown oily portion of the distillate appeared to consist mostly of mesityl oxide.

It is evident, therefore, that ethyl alcohol, if formed, is at once oxidised. This is not surprising when it is remembered that alkalis can act as oxidising agents at high temperatures. One might imagine that the ethyl alcohol is first oxidised to acetic acid, which then loses water and carbon dioxide, giving acetone. This, by condensation of two molecules losing water, would give mesityl oxide, thus,—

$$CH_3COCH\boxed{H_2O}C{<}^{CH_3}_{CH_3} =$$

$$= CH_3{-}CO{-}CH = C{<}^{CH_3}_{CH_3} + H_2O$$

Mesityl oxide.

Soda-lime acts as a powerful dehydrating agent. A similar experiment with citric acid gave the same products. In this case the theoretical product is isopropyl alcohol,—

$$\begin{array}{l} CH_2.CO.OH \\ | \\ C(OH).CO.OH + 6NaOH \\ | \\ CH_2.CO.OH \end{array} = \begin{array}{l} CH_3 \\ | \\ CHOH \\ | \\ CH_3 \end{array} + 3Na_2CO_3 + 3H_2O$$

Citric acid. Isopropyl alcohol.

This by oxidation gives acetone, which then undergoes condensation, giving mesityl oxide.

It is thus evident that in these pyrogenic reactions the theoretical first products are only formed, when they are highly stable compounds (such as saturated hydrocarbons). Otherwise oxidation and dehydration occur. A fact to be noted is that very little charring takes place during the heating.

Time did not permit of further experiments with other hydroxy acids being carried out, especially as the results obtained were, on the whole, negative.

University College, Gower Street, W.C.

Dextro-camphorates of Potassium.—E. Jungfleisch and Ph. Landrieu.—The authors have prepared and studied the properties of the following four compounds of potassium and camphoric acid:—Dipotassium *d*-camphorate, monopotassium *d*-camphorate, monopotassium *d*-dicamphorate, and monopotassium *d*-tetracamphorate. The first of these is very stable and is not decomposed by water, while the others are very unstable in presence of water and decompose to give the dipotassium camphorate and camphoric acid.—*Comptes Rendus*, clvii., No. 19.

COLUMBIUM v. NIOBIUM.

The Editor has received the following communication and letter from Prof. F. W. Clarke:—

Dear Sir William,—I enclose a brief note which I should like to have inserted in the Chemical News. I think English chemists should stand up for their countryman.—Yours sincerely,

F. W. Clarke.

At a meeting of the Council of the International Association of Chemical Societies in Brussels last September a Committee on Inorganic Nomenclature, among other recommendations, endorsed the name and symbol "niobium" and "Nb" for the element which was originally named columbium. As this recommendation is historically erroneous, a brief statement of the facts appears to be desirable.

In 1801, Hatchett, an English chemist, analysed a strange American mineral, and in it found a new metallic acid; the oxide of an element which he named columbium. A year later, Ekeberg, in Sweden, analysed a similar mineral from Finland, and discovered another element, which he called tantalum. Wollaston, in 1809, undertook a new investigation of these elements, and concluded that they were identical; a conclusion which, if it were true, would have involved the rejection of the later name and the retention of the earlier columbium. The accepted rules of scientific nomenclature make this point clear.

For more than forty years after Hatchett's discovery both names were in current use; for although Wollaston's views were accepted by many chemists there were others unconvinced. In 1844, however, Heinrich Rose after an elaborate study of columbite and tantalite from many localities, announced the discovery of two new elements in them, niobium and pelopium. The latter supposed element was afterwards found to be non-existent, but the niobium was merely the old columbium under a new name. That name in some mysterious manner was substituted by the German chemists for the original appropriate name, and has been in general use in Europe ever since. In America the name columbium has been generally preferred, and was formally endorsed by the Chemical Section of the American Association for the Advancement of Science more than twenty years ago. In England also columbium is much used, as, for example, in Roscoe and Schorlemmer's "Treatise on Chemistry," Thorpe's "Dictionary of Applied Chemistry," and the new edition of the "Encyclopædia Britannica."

The foundation of Rose's error seems to have been an uncritical acceptance of Wollaston's views; for he speaks of all the minerals he studied as tantalite. He also, at least in his original memoir, claims that the atomic weight of niobium is greater than that of tantalum, and here he was obviously wrong.

In short, the name columbium has more than forty years priority, and during that interval was accepted by many chemists, and was more or less in current use. To employ the name niobium is not only unhistorical, but it is also unfair to the original discoverer, meaningless, and without any justification whatever. Furthermore, it injures the splendid reputation of Rose, for it perpetuates and emphasises one of his few errors. The recommendation of the Committee above mentioned should not be accepted, for it is opposed to the established rules of priority.

Fluorine as a Constant Constituent of the Emanations from the Earth's Core.—Armand Gautier.—Fluorine is always found to be present when the following are examined:—The minerals formed in crystalline rocks, thermal springs, emanations from the soil, volcanic gases, and gases from solfaturi. All these products have a very deep-seated origin. Other elements also frequently accompany it, viz., boron, sulphur, nitrogen, arsenic, chlorine, bromine, iodine, silicon, carbon (as CO_2), sodium, free hydrogen, copper, &c.—*Comptes Rendus*, clvii, No. 19.

THE SCIENTIFIC WEEK.

(*From Our Own Paris Correspondent*).

Apparatus for Testing Metals by Impingement or Shock.

The testing of metals by impingement presents practical difficulties that have been the object of a recent study by MM. G. Charpy and Cornu. These scholars have understood that, in order to obtain a comparison between metallic bars in spite of inevitable local inequalities, it is necessary to impress them with very feeble deformations, very inferior to those that might determine the beginning of a rupture. Tests have been made with a view of discovering if, in operating on un-notched bars, the defect by flexion with the beetle pendulum gave the same identical results, concordant with each other. The tests were made with a beetle or ram-pendulum of 30 kilogs. with a fall of 1·314 metres, and with a pendulum of 300 kilogs. with a fall of 3·197 metres. The relative average error was, in the first case, of 1·4 per 100; in the second case, of 1·0 per 100; that is to say, that the practical identity of the results may be reckoned upon. All the same it is most necessary to take into account the friction against the angular props, and, for both knives and props, to adopt a very rigorously defined form, presenting no acute angles.

Studies on the Radio-activity of Meteorological Waters.

A learned physicist, M. Munzo del Castillo, with the help of several collaborators, has effected a certain number of researches concerning the radio-activity of waters of different sources which have led to extremely interesting results. He has remarked that rain-water collected in winter contained a notable proportion of emanation which went on gradually decreasing, as well as a certain quantity of ions that had entirely disappeared at the end of twelve days. Snow that had fallen in Madrid in February also showed a pretty well marked radio-activity. The same physicist has measured the activity of the air of the sub-soil. To extract it he introduced into ditches of two metres deep, at different depths, apparatus formed of a horizontal square surmounted by a cylinder that was filled with little stones and that communicated with the outside by a vertical iron tube; thus at any moment air could be extracted from the sub-soil. The measures and observations taken in autumn have shown that there is no relation between the compared activities of the air of the sub-soil and atmospherical air. The activity of the air of a sub-soil of pretty hard consistence appears to be greater than that of a soft sub-soil. Down to two metres beneath the surface the radio-activity increases with the depth. Other determinations, effected in winter on the compared activities of the air of the sub-soil and of atmospheric air, have enabled it to be observed, besides, that the variations of pressure and of radio-activity of the air of the sub-soil are of the same sense as those of atmospheric air, and that the temperature and direction of the wind do not appear to exercise any influence on the radio-activity of the sub-soil. Lastly, M. del Castillo has also taken measures of the radio-activity of several Spanish mineral water springs, and he has noticed a certain activity for the waters of Rivas (Gerona), of Caldas de Juy (Pontevedra), of the Sierra Juanaanta (Murcia), and of Garganton (Guadarrama).

Metallic Coatings.

M. P. Nicolardot has just made an interesting communication to the Academy of Sciences on the "Actual State of Industrial Metallic Coatings." Of all the processes proposed to obtain metallic coatings on the surface of objects, metallic or not, only three have become really industrial. They are:—First, dipping into a bath of molten metal; second, electrotyping; third, the Schoop process. M. Nicolardot describes these processes, and shows how they are practised. The only metals with which objects of iron or copper can be plated by a simple dipping are zinc, lead, and tin. The process succeeds only because they form alloys with the underlying metal. The practice of this process requires the employment of considerable quantities of melted metal (as much as 10 cubic metres) in one workshop. This is a cause of very serious accidents that often occur when hollow objects or objects insufficiently dried after scouring are plunged into the melted metal. No way has been found up till the present time to completely suppress these accidents. The process, in spite of the improvements it has received, give irregular coatings of unequal adherence and thickness. Considerable quantities of metal are consumed, some of it passing into the coating that is always thicker than is necessary, and some into the dross which it partly transforms. Lastly, the working of the process necessitates the employment of a considerable plant, and the temperature of the bath must not exceed 500°; moreover, the plated pieces undergo a second annealing and are sometimes deformed. For all these reasons many trials have been made to obtain metal platings in different manner. Electrolysis only gives a partial solution to the problem, for it can only be performed on objects of rather small dimensions. By this process all the usual metals, excepting lead and aluminium, can be deposited. By different means trials have been made to improve the adherence, the coherence, the compactness, and the regularity of electrolytic deposits, but with only partial success. M. Nicolardot explains the reason of this, and shows the impossibility of obtaining a perfect result. Indeed, the deposit is the result of a veritable bombardment of molecules. They are thrown from one of the electrodes to the other, and their passage is such that the deposits on the planes are always circular or elliptic rings. The superposition of these rings and their displacement gives to the final deposit an alternatively increasing or diminishing thickness, following certain laws, and it is their great number that gives the illusion of their uniformity. The third process, that of Schoop, in its present form consists in projecting violently on to the object the metal for the coating in the form of a very fine powder. For this a pistol is employed. Through this pistol, held in the hand, there is passed a wire of the metal. This wire is heated by an oxyhydric pipe placed within the pistol; then whether the metal has been very strongly heated or whether it has been transformed into a liquid or solid dust, it is driven only by a violent draught, the shaft of which is part of the pistol. The rapid success of this rather new process is explicable by its great convenience and its universality. It can, in fact, be applied to all metals and may be employed to coat all substances, wood, wax, paper, stuffs, lace; it is without danger. Lastly, strange to say, it does not essentially differ from electrolysis. It also acts by bombardment, and the adherence of the deposit can be explained in the same way, as is admitted by M. Nicolardot. In both cases the metal deposited is strongly cold-hammered, and seems to appear in a new allotropic state. M. Nicolardot shows the advantages to be drawn from the porosity of certain deposits obtained by the Schoop process to increase, for example, the resistance to certain corrosive agents; he indicates its application to cementation, to obtain reserves, for the reproduction of mouldings, of phonographic discs, of trichromatic clichés, &c.

Subterranean Fire in the Coal Fields of Decazeville.

Layers of coal are always in combustion in the coal bed of Decazeville, particularly between that place and Cransac, over a length of about 6 kilometres. At Decazeville in the great basin in which the Commentry-Fourchambault-Decazeville Company, in the open air, works a layer

of 50 metres thick, the least crack in connection with the deep ground sends forth an abundance of smoke. More to the south, at Combes, thirty or forty years ago, the flames issuing from the cracks of the mountains illuminated all the country round during the night. Since then the intensity of this furnace has decreased; nevertheless it is still in activity, the ground is burning hot, and when it rains the mountain is enveloped in mist and steam. A part of the ground to the north of Cransac is called the Etuve (vapour-bath or oven). By digging down into the soil for a dept of 50 centimetres you arrive at an oven of 50°. There was formerly a mineral magnesium spring there, and these natural baths or ovens were employed in the treatment of certain maladies. After the tracing of the galleries of the mines the spring disappeared. However, there is another one of the same kind at Combes. Quite lately, as has been reported by M. G. Patrouilleau, the presence of the subterranean fire to so very far from the surface has been remarked in the town of Decazeville itself. Some workmen who were digging in one of the streets of the town a cutting for laying an armoured cable of 3000 volts, remarked with surprise that, for a length of about 20 metres at about 1 metre's depth, temperature rose to 75° C. The cable was laid, armoured, and isolated by paper, by suspending it in a kennel with lateral chimneys or aeration. From the upper chimney hot air and large quantities of steam come forth. According to the inhabitants of the town this elevation of temperature might have been foreseen, for indeed in the portion of the street under consideration the snow does not lay and the rain water is quickly evaporated. M. Patrouilleau says that from the calcined vestiges found in the basin the fire is in a state of retrogression, but the layers of coal intact are so powerful and so close together that an extension of the scourge, due to subterranean landslips, for example, is always to be feared.

THE ZODIACAL MATTER AND THE SOLAR CONSTANT.

The existence of little intermercurial planets may be revealed by the observation of the perturbations that their masses determine, as well as by the reflection of the solar light and by occultations at periodic intervals. In particular the long periodic inequalities that are to be met with in the theory of the moon may be explained by the existence of a swarm of little intermercurial planets circulating near the sun (Radan, Shint, Blancat). Lastly, the fact that in the month of March the southern edge of comets is brighter than the northern edge, which is further removed from the earth, may be explained by admitting that the zodiacal light represents the elliptic projection of concentric rings crossed by swarms of planets. The passage of these swarms twice a year, in May and November, before the sun seems to be accompanied, according to MM. Abbot, Towle, and Aldrich, by slow and periodic variations of the solar constant, amounting to 5 per 100 in about from seven to ten days.

Colloidal Properties of Meta-hæmoglobin. Modification of Viscosity and Surface Tension of Suspensions by HCl and NaOH.—Filippo Bottazzi.—An aqueous suspension of pure meta-hæmoglobin has about the same viscosity and surface tension as distilled water. When, under the action of HCl or NaOH, the meta-hæmoglobin passes into solution the viscosity of the liquid increases and the surface tension diminishes, the reverse taking place when the acid or alkali is neutralised. When the viscosity has been increased by the addition of HCl it begins to decrease if an excess of acid is added. The addition of sodium chloride produces a small but constant diminution of the surface tension. The lowering of the surface tension depends principally on the undissociated molecules of protein.—*Atti della Reale Accademia dei Lincei*, xxii [ii.], No. 6.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, December 11th, 1913.

SIR WILLIAM CROOKES, O.M., President, in the Chair.

PAPERS were read as follows:—

"*Intermittent Vision.*" By A. MALLOCK, F.R.S.

When a wheel turns so rapidly that the separate spokes cannot be seen or easily followed by the eye, and if at the same time the observer receives a small mechanical shock of almost any kind, the spokes appear almost stationary for a fraction of a second.

The appearances depend on the speed of rotation, on the brightness of the illumination, and, to a lesser degree, on the nature of the shock.

Suitable shocks are given by the contact of the feet with the ground as in walking, by tapping the head or body, and in many other ways.

The convention by which rapid rotation is indicated in drawings, namely, that of introducing a large number of radial lines in place of the actual spokes, probably has its origin in one form of the same phenomenon.

In the paper some experiments are described bearing on the relation between the appearances and the speed of rotation, and an explanation is suggested depending on an assumed variation of sensibility produced by a slight shock. This variation, which it appears is rapidly extinguished, has a periodic time of about 1/18 second, but this differs slightly for different individuals.

"*Attempts to Observe the Production of Neon or Helium by Electric Discharge.*" By Prof. the Hon. R. J. STRUTT, F.R.S.

The present experiments were begun in the hope of confirming the work of Collie and Patterson (*Trans. Chem. Soc.*, 1913, ciii., 419; and *Proc. Chem. Soc.*, 1913, xxix., 217). The results have been negative, whether from a failure to appreciate the proper conditions for the production of neon by electric discharge through hydrogen or from some other cause.

The test for neon was carried out so that the amount found in 1/100 cc. of air could easily be detected.

It was found difficult or impossible to be sure of excluding air, when the hydrogen was pumped out from one apparatus and transferred to another by pneumatic trough manipulation.

This kind of manipulation was avoided. The hydrogen, after each experiment, was converted into water by admitting a little oxygen into the discharge vessel and continuing the discharge for a short time at intervals. The resulting water vapour was frozen out in a side tube cooled by liquid air. Diffusion was free enough to soon remove the whole of it, and a pure oxygen discharge remained. The oxygen could easily be removed by cooled charcoal. Thus the entire series of operations were carried out in one closed apparatus. The discharge with electrodes in a cylindrical tube was tried, both at the cathode-ray stage and at higher pressures; also the electrode-less discharge. The duration of each experiment varied from 8 to 20 hours. In no case was any trace of neon observed.

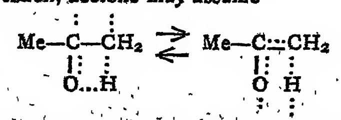
"*The Relations between the Crystal-symmetry of the Simpler Organic Compounds and their Molecular Constitution.*" Part III. By WALTER WAHL.

"*The Selective Absorption of Ketones.*" By Prof. G. G. HENDERSON and I. M. HEILBRON.

Many aliphatic ketones containing one of the groups —CH_2.CO— or —CO.CO—, as well as their derivatives, absorb selectively in the visible and ultra-violet regions. Some at least of them exist in keto and enol modifications, R.CH_2.CO.R′ and R.CH:C(OH).R′, and according to one hypothesis their absorption is due to some intramolecular vibration which occurs when one tautomeric form changes

into the other. Recent work, however, has shown that aliphatic ketones of the type R.CO.R′ are entirely ketonic in form, no trace of an enol modification being present; further, it has been proved that the absorption of ethyl aceto-acetate, which can exist in both forms ($CH_3.CO.CH_2.CO_2Et$ and $CH_3.C(OH):CH.CO_2Et$), is independent of any keto-end oscillation. Hence it is improbable that this form of oscillation is the cause, even indirect, of selective absorption.

The authors have found that the selective absorption of a large number of simple ketones is of the same type, since the absorption bands of all are practically identical. They suggest that the absorption of these compounds may be due to electronic disturbances accompanying oscillations which arise from the alternate formation and breaking down of unstable ring systems within the molecule. For example, the following figures indicate the two phases (each having only a momentary existence) which, according to this suggestion, acetone may assume—



This idea of intramolecular oscillation arising from momentary ring formation can be extended to embrace other groups of ketones, the type of ring formed varying with the constitution of the compound.

"*Absolute Measurements of a Resistance by a Method based on that of Lorenz.*" By F. E. Smith.

The instrument employed differs from all other forms of apparatus based on the method of Lorenz, inasmuch as two discs are employed instead of one. The disturbing effect of the earth's magnetic field is thus practically eliminated.

The magnetising coils are four in number; they are wound in single layers on marble cylinders, and the disposition of coils with respect to discs is such that the resulting magnetic fields through the discs are opposed in direction, and the intensity of the field at points in the neighbourhood of the edge of a disc is of zero value, or nearly so.

Each of the two discs supports ten insulated bronze segments placed at equal distances around its circumference, and the ten segments on one disc are connected to those on the other disc by ten conducting wires passing through the centre of the shaft. When the wires rotate a difference of potential is produced between their ends. These differences of potential may be placed in parallel or in series and balanced against that on a standard resistance R through which the same current flows as through the coils. The resistance R can thus be found in terms of mutual inductance of coils and brush-contact circles and rate of rotation of conductors.

The brushes consist of thin phosphor bronze wires stretched by spiral springs, and resemble violin bows. Petrol is employed as a lubricant for the brushes. Speed is maintained constant by an electrical method.

The result of the experiments is that a resistance of one international ohm is equal to $1{\cdot}00052 \pm 0{\cdot}00004$ ohms (10^9cm./sec.).

"*A Determination of the Electromotive Force of the Weston Normal Cell in Semiabsolute Volts.*" By A. N. Shaw. (With a Preface by Prof. H. L. Callendar, F.R.S.)

This paper represents the completion of work commenced by Prof. H. L. Callendar and Mr. R. O. King in the years 1894 to 1898. The E.M.F. of the Weston Cell was balanced against the P.D. on a standard ohm due to a current of about 1 ampère measured by means of an electrodynamometer of the type described and figured by Clerk Maxwell ("Electricity and Magnetism," vol. ii., p. 339). The original electrodynamometer proved defective in rigidity of the frame and suspension, and in insulation of the coils, the dimensions of which could not be measured with sufficient accuracy. The coils were rewound with a double winding, affording a perfect check on the insulation. The mean radius of the large coils was determined by winding with a measured length of hard-rolled copper tape, graduated on a 50 foot comparator. These coils were also made reversible and interchangeable, in order to eliminate small residual errors of symmetry in determining the mean distance between their planes. The constant of the suspended coils was determined by a null method of comparison with the large coils. A duplex method of reading the deflections was devised, giving an order of accuracy approaching 1 in 100,000. The bifilar suspension was modified so that the control depended mainly on gravity, but there remained a small correction amounting to about 3 parts in 10,000 due to the imperfect elasticity of the suspending wires. The work of reconstructing the apparatus was performed entirely by Mr. King, during 1897—8, under the supervision of Prof. Callendar, who published an account of the preliminary observations made with the apparatus in his paper on "Continuous Electrical Calorimetry" (*Phil. Trans.*, A, 1902, p. 89).

The present author, holding a scholarship endowed by Mr. King, has repeated and verified Mr. King's measurements and results, and has extended the observations and calculations up to the limit of accuracy attainable with the apparatus. In particular, he has been able, by a careful study of Mr. King's suspension (*Phil. Mag.*, 1912), to determine the correction for imperfect elasticity within very narrow limits. The final result for the E.M.F. of the Weston Cell in semi-absolute volts by this method comes out 1·01827 at 20° C., which agrees closely with the mean of the best recent determinations, namely, 1·01824. The agreement is of interest because the method presents so many radical points of difference from the majority of those recently employed.

"*Elastic Hysteresis in Steel.*" By F. E. Rowett.

A thin-walled steel tube was coupled to a coaxial tube of greater section and length. The compound tube was twisted, and the twist in each component measured by spirit levels. The twist of the large tube, in which the stress and therefore also the hysteresis was small, measured the torque applied to the small tube. Strains of the order 10^{-6} were measured in this way, and the energy dissipated by elastic hysteresis during a cycle of stress a little within the elastic limit determined within $2\frac{1}{2}$ per cent. The dissipation was observed when the same tube was subjected to similar stress cycles at a rate of 60 per second. For this purpose the tube was fixed at one end, a fly-wheel mounted on the other, and the rate of decay of torsional oscillations was observed photographically. The energy dissipated per cycle was found to be the same as in the static experiment. The elastic hysteresis in hard drawn tubes was about one-eighth of that in the same tube after annealing.

"*A Simple Form of Micro-Balance for Determining the Densities of Small Quantities of Gases.*" By F. W. Aston.

1. A simple micro-balance is described, by which the densities of gases may be determined relative to some standard gas, using a null method.

2. About half a cubic centimetre only of the gas is required.

3. The determination can be performed in a few minutes, with an accuracy of 0·1 per cent.

4. Possibilities of its use in other fields of research are indicated.

"*On a Second Spectrum of Neon.*" By T. R. Merton.

The Spectrum of Neon has been investigated under different conditions of electrical excitation. It has been found that with a condensed discharge a second spectrum is developed, as in the case of Argon, Krypton, and Xenon. The strongest lines of the ordinary spectrum are also feebly visible when a condensed discharge is used.

CHEMICAL SOCIETY.

Ordinary Meeting, November 6th, 1913.

Prof. W. H. PERKIN, LL.D., F.R.S., President, in the Chair.

(Concluded from vol. cviii., p. 317).

274. "*The Action of Chlorine on* m-*Iodoaniline and on* m-*Bromoaniline*," By HAMILTON MCCOMBIE and PERCY JAMES WARD.

When *m*-iodoaniline is chlorinated in glacial acetic acid solution, 2 : 4 : 6 *trichloro*-3-*iodoaniline* is produced. Under no conditions could an iododichloride be obtained; this is contrary to the experience of Willgerodt and Wikander (*Ber.*, 1007, xl., 4068), who considered that they obtained an unstable iododichloride. When 2 : 4 : 6-trichloro-3-iodoaniline is treated with alcoholic ethyl nitrite, 2 : 4 : 6-trichloroiodobenzene is produced, which has been described previously by several observers. 2 : 4 : 6-Trichloro-3-iodoaniline could not be converted into a hydrochloride, nor could it be benzoylated in presence of sodium hydroxide.

The acyl derivatives of *m*-iodoaniline showed a slight tendency to the formation of iododichlorides, but these proved to be very unstable, and readily yielded ring substitution products.

The prolonged action of chlorine on *m*-iodoaniline resulted in the formation of 2 : 2 : 3 : 4 : 4 : 6-*hexachloro*-5-*iodo*-Δ^3-*cyclohexenone*, $CCl_2<\begin{matrix}CHCl.CCl_2\\ Cl\!=\!\!=\!\!=\!CCl\end{matrix}>CO$. In this reaction the amino-group has been removed in the form of ammonium chloride, whilst the iodine atom still remains in the molecule. The constitution of this ultimate chlorination product is based on the following reactions:—1. On treatment with potassium iodide, the compound yields 2 : 4 : 6-trichloro-3-iodophenol. 2. On treatment with potassium acetate in the presence of acetic acid, there results 2 : 3 : 4 : 6-tetrachloro-5-iodophenol. 3. Concentrated sulphuric acid converts the compound into 2 : 3 : 6-trichloro-5-iodo-*p*-benzoquinone.

Analogous results have been obtained on chlorinating *m*-bromoaniline under the same conditions as were employed for the iodo-compound.

275. "*Guanidinium Nitrite and its Decomposition by Heat.*" By PRAFULLA CHANDRA RAY, MANIK LAL DEY, and SARAT CHANDRA JANA.

Guanidinium nitrite, from the conductivity measurement of its aqueous solution, is found to behave like a typical alkaline nitrite with two ions.

When heated, guanidinium nitrite yields ammonia, hydrocyanic acid, nitrogen monoxide, and nitrogen among the gaseous products, and leaves a residue which was proved to be melamine.

276. *The Absorption of Light by Uranous Chloride in different Solvents.*" By THOMAS RALPH MERTON.

The absorption spectra of uranous chloride solutions in different solvents have been investigated, more especially in the presence of free hydrogen chloride. In some cases the presence of a small quantity of water produces a marked change in the absorption spectrum. It is concluded that the vibrators responsible for different bands or groups of bands are situated in different molecular aggregates.

277. "*The Influence of Solvents on the Rotation of Optically Active Compounds.* Part XIX. *The Rotation of certain Derivatives of Lactic Acid.*" By THOMAS STEWART PATTERSON and WILLIAM COLLINS FORSYTH.

The rotation of several derivatives of lactic acid has been examined, over a range of temperature, both in the homogeneous state and in solution in two solvents, which usually differ widely in their action.

278. "*The Action of Nitrogen Iodide on Methyl Ketones.*" By FREDERICK DANIEL CHATTAWAY and ROBERT REGINALD BAXTER.

Ketones containing a methyl group react very readily with nitrogen iodide, iodoform, ammonia, an acid, and an amide being formed, In the reaction the methyl group appears to be completely substituted by iodine, a tri-iodomethyl ketone being formed, which in presence of the ammonia simultaneously set free is hydrolysed to iodoform and an acid. a similar reaction between the substituted ketone and ammonia leading to the formation of iodoform and an amide. The reactions may be formulated thus:—

$$R{\cdot}CO{\cdot}CH_3+NH_3{\cdot}NI_3 = R{\cdot}CO{\cdot}CI_3+2NH_3.$$
$$R{\cdot}CO{\cdot}CI_3+H_2O = R{\cdot}CO_2H+CHI_3.$$
$$R{\cdot}CO{\cdot}CI_3+NH_3+R{\cdot}CO{\cdot}NH_2+CHI_3.$$

The reaction between nitrogen iodide and acetone particularly striking, as the black solid in a few minutes is apparently transformed into a bright yellow one.

279. "*Note on the Constituents of Commercial Chrysarobin.*" By FRANK TUTIN and HUBERT WILLIAM BENTLEY CLEWER.

In a recent communication (*Trans.*, 1912, ci., 290) the authors described the results of the examination of several samples of commercial chrysarobin. During the course of this research the following substances were isolated:—Chrysophanol ("chrysophanic acid"), $C_{15}H_{10}O_4$; emodin monomethyl ether, $C_{16}H_{12}O_5$; chrysophanolanthranol, $C_{15}H_{12}O_3$; dehydroemodinanthranol monomethyl ether, $C_{16}H_{12}O_4$; ararobinol, $C_{23}H_{16}O_5$; and emodin, $C_{15}H_{10}O_5$.

It was furthermore pointed out that commercial chrysarobin is subject to considerable variation in the relative proportions of its constituents, some samples being even entirely devoid of certain compounds which occur in others. In all the products examined, however, the first four of the above mentioned compounds were invariably found to be present.

Very shortly after the appearance of the above communication a paper on the same subject was published by O. Hesse (*Annalen*, 1912, ccclxxxviii., 65). The results described in the latter paper, however, are such as would give the impression, at first sight, that the conclusions of Hesse and those of the present authors had very little in common. Some further explanation of the subject therefore appears desirable.

Hesse mentions as constituents of commercial chrysarobin the following substances:—"Chrysophanol" (see Note) (chrysophanolanthranol); "emodinol" (emodinanthranol); the methyl ethers of both these substances; and a new substance, $C_{15}H_{12}O_4$, which is designated as chrysarobol. It is stated by Hesse, however, that of these five substances, only two, namely, "chrysophanol" (chrysophanolanthranol) and chrysarobol, had been isolated directly in a pure state from commercial chrysarobin, whereas all the constituents described by the present authors were directly isolated in a state of purity.

(NOTE.—It would appear unfortunate that Hesse should have employed the name chrysophanol for the anthranol of "chrysophanic acid," since the former name had already been employed by the present authors (*loc. cit.*, p. 292), and previously by Tschirch (*Arch. Pharm.*, 1911, cclxix., 222, and 1912, ccl., 27), as the designation for pure "chrysophanic acid." Moreover, since Hesse himself (*Annalen*, 1899, cccix., 32) and Jowett and Potter (*Trans.*, 1902, lxxxi., 1577) have previously applied the name "chrysarobin" to chrysophanolanthranol, the employment of yet a third name for this substance only adds to the confusion already existing).

Chrysophanolanthranol has long been known to be a constituent of commercial chrysarobin, but chrysarobol has not been obtained by the present authors. This is doubtless due to the varying composition of the com-

mercial product, since Hesse remarks that he only obtained this new substance from the chrysarobin occurring in commerce in the years 1905 and 1906.

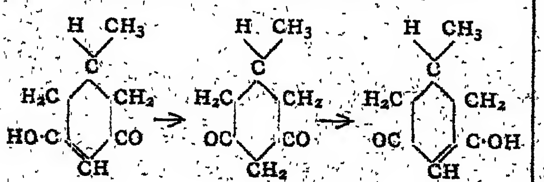
With regard to emodinanthranol (Hesse's "emodinol"), no doubt can be entertained that this was derived chiefly from the monomethyl ether of dehydroemodinanthranol (see Note) which was isolated and described by the present authors, since the material examined by Hesse had been heated with hydriodic acid. Hesse himself shows that he could not obtain "chrysophanol methyl ether" and "emodinol methyl ether" in a state of purity, and the evidence he adduces does not seem to justify the conclusion that they are present. In the material examined by the present authors, the former compound certainly did not occur, but proof of the presence of small amounts of the latter was obtained.

The statement made by Hesse that chrysophanol-anthranol (Hesse's "chrysophanol") is insoluble in alkalis in the absence of air is incorrect. This substance dissolves fairly readily in 10 per cent aqueous potassium hydroxide, yielding a bright yellow solution, which, on the admission of air, develops the deep red colour due to the formation of chrysophanol.

[NOTE.—In a footnote to his paper, added after the completion of the work, Hesse states that he has never observed the occurrence of the monomethyl ether of dehydroemodinanthranol described by the present authors, but this is obviously due to his having worked almost entirely with material which had been demethylated by means of hydriodic or hydrochloric acid. In all the commercial samples of chrysarobin examined by the present authors it was present to the extent of from 13·4 to 41·1 per cent).

280. "*Substituted Dihydroresorcins. 1-Methyldihydroresorcin and 2-Methyldihydroresorcin.*" By CHARLES GILLING.

1-Methyldihydroresorcin is a tautomeric substance, and it is suggested that this tautomerism prevents the existence of the two stereoisomeric forms, since it is apparent that I. and II. are mirror images of each other:—



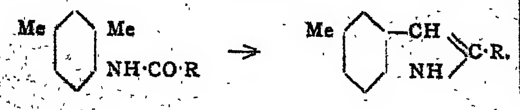
I. II.

The replacement of the labile hydrogen atom by an ethyl group destroys this tautomerism, and the ethyl ether can accordingly be isolated in two distinct forms.

2-Methyldihydroresorcin can be prepared from cresorcinol by reduction, but the product so obtained is impure, and it was only isolated in the form of crystalline derivatives.

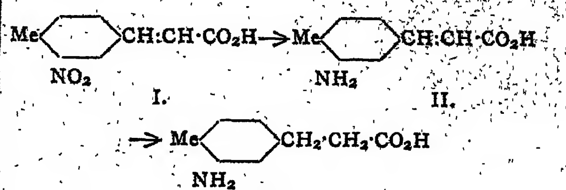
281. "*Researches on the Constitution of Physostigmine. Part III. The Formation of Substituted Indoles from* m-4-*Xylidine, and the Reduction of 3-Nitro-p-tolylacrylic Acid.*" By ARTHUR HENRY SALWAY.

In this investigation the author has described some experiments, which were conducted with the object of ascertaining whether Madelung's reaction for the preparation of substituted indoles from *o*-toluidides (*Ber.*, 1912, xlv., 1128, 3541) could be applied to acyl derivatives of *m*-4-xylidine, according to the scheme:—



It has now been shown that aceto-*m*-4-xylidide readily yields 2:5-dimethylindole by this method. The reaction, however, was found not to be generally applicable since 2:4 *xylylsuccinamic acid*, $C_6H_3Me_2{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$, and its derivatives, which were of interest in connection with the problem of the constitution of physostigmine, could not be converted into indoles without disruption of the molecule.

The reduction products of 3-nitro-*p*-tolylacrylic acid (I.) have also been described. It has been ascertained that the nitro-group of this substance is more readily attacked by reducing agents than the cinnamyl residue, so that the first product of the reaction is 3-*amino-p-tolylacrylic acid* (II.), which by further reduction is converted into β-3-*amino-p-tolylpropionic acid* (III.):—



I. II. III.

282. "*Mechanism of the Decomposition of Carbamide and Biuret by Heat, and of the Formation of Ammelide.*" By EMIL ALPHONSE WERNER.

In continuation of work recently published (*Trans.*, 1913, ciii., 1010), a quantitative study of the decomposition of carbamide and biuret by heat has been made, the results of which have thrown new light on the mechanism of the progressive changes.

It was shown that the formation of biuret by the action of heat on carbamide is a reversible reaction in accordance with the equation:—

$$HN{:}C{<}^{NH_2}_{OH} + HN{:}CO \underset{\text{above } 190^\circ}{\overset{135-150^\circ}{\rightleftarrows}} \begin{array}{c} HN{:}C{\cdot}OH \\ | \\ NH \\ | \\ HN{:}C{\cdot}OH \\ \text{(enol).} \end{array} \xrightarrow{\text{biuret}} \begin{array}{c} CO{\cdot}NH_2 \\ | \\ NH \\ | \\ CO{\cdot}NH_2 \\ \text{(keto).} \end{array}$$

By heating pure anhydrous biuret for five minutes at 192° (m. p. 190°), as much as 30 per cent of regenerated carbamide was extracted from the residue. The general idea that biuret decomposes directly into ammonia and cyanuric acid is therefore erroneous.

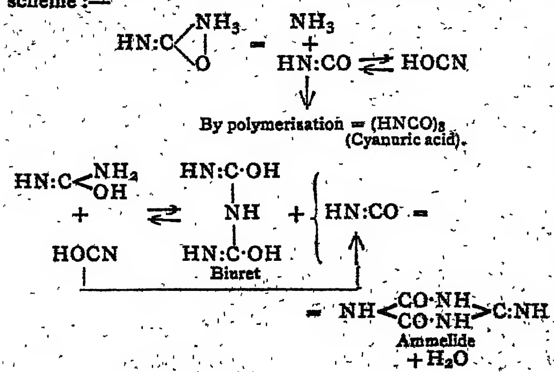
No evidence could be obtained of the formation of tricyanocarbamide, $C_3N_3(NH{\cdot}CO{\cdot}NH_2)_3$, described by Hantzsch and F. Hofmann (*Ber.*, 1905, xxxviii., 1010) as a product of the action of heat on carbamide; the properties of the substance described by them are identical with those of ammelide (cyanuric monamide), which has been long since recognised by Liebig and Wöhler and others as a product of the decomposition of carbamide. Proof was obtained that this compound originates from the further interaction of cyanic acid and biuret according to the equation:—

$$HN{<}^{CO\cdot NH_2}_{CO\cdot NH_2} + HN{:}CO = HN{<}^{CO\cdot NH}_{CO\cdot NH}{>}C{:}NH \text{ or}$$

$$HN{<}^{CO\cdot NH}_{CO-N}{\geq}C{\cdot}NH_2 + H_2O,$$

and hence is also formed during the decomposition of biuret, but in smaller quantity, since the conditions are less favourable. Thus it was shown that the whole cycle of changes which take place during the decomposition of carbamide and biuret by heat can be simply explained by

(1) dissociation, and (2) instability and reactivity of nascent cyanic acid, as illustrated by the following scheme:—



283. "*Note on the Mechanism of a Bromination in Ketones.*" By Arthur Lapworth.

H. Leuchs has recently found that, by bromination of an optically active ketonic acid, a monobromo-derivative is obtained which exhibits some optical activity. As the activity of both compounds is dependent on enantiomorphism in the arrangement of the atoms and groups around the α-carbon atom to which the bromine attaches itself, Leuchs concludes that the enolic form of the ketone could not have been an intermediate stage in the substitution process, and he suggests applying a similar test to active monalkylmalonic hydrogen esters (*Ber.*, 1913, xlvi., 4238).

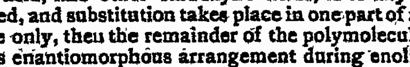
Leuchs's inference is not quite conclusive, for the facts admit of different interpretations; for example, if the ketonic acid, like other carboxylic acids, is to any extent associated, and substitution takes place in one part of a polymolecule only, then the remainder of the polymolecule may retain its enantiomorphous arrangement during enolisation of the first portion, and consequently the formation of a new "asymmetric" carbon atom in the latter would naturally lead to the formation of some excess, however small, of atoms of one sign. In other words, a "partial asymmetric synthesis" is possible.

The bromination of active α-methylbutyric acid has previously been studied by Schütz and Marckwald (*Ber.*, 1896, xxix., 59), and of β-phenyl*iso*butyric acid by Lapworth and Lenton (*Proc.*, 1902, xviii., 35). In both instances the product was inactive.

284. "*Studies in the Diphenyl Series.* Part V. *Derivatives and Substitution Products of the Two Isomeric o-Dinitrobenzidines and Synthesis of Derivatives of Benzerythrene.*" By John Cannell Cain, Albert Coulthard, and Frances Mary Gore Micklethwait.

The authors have prepared a number of acyl and azo-derivatives of the two isomeric *o*-dinitrobenzidines (*Trans.*, 1912, ci., 2298), and have submitted the two bases to the diazo-reaction.

3:3'-Dinitrobenzidine gives the corresponding disubstituted 3:3-dinitrodiphenyl, but 3:5'-dinitrobenzidine, in those cases where copper is employed, gives derivatives of benzerythrene:—



Of the numerous derivatives of the two bases that have been prepared, no two corresponding ones are identical.

285. "*Harmine and Harmaline.* Part II. *The Synthesis of iso-Harman.*" By William Henry Perkin, jun., and Robert Robinson.

A detailed description of work of which a preliminary account has already appeared (*Proc.*, 1912, xxviii., 154).

NOTICES OF BOOKS.

Researches on Irritability of Plants. By Jagadis Chunder Bose, M.A., D.Sc., C.S.I. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1913.

The experiments described in this book are exceedingly interesting, and the author appears to have arrived at results of vital importance in biochemistry. He has devised and perfected two pieces of apparatus which he calls the Resonant and Oscillating Recorder respectively, by means of which the amplitude and period and also the absolute rate of movement of the plant during any phase of autonomous response to stimulation can be determined with perfect accuracy. He has found it possible to record time-intervals which do not exceed one-thousandth of a second in length. The so-called sensitive plants were chosen for study, and mechanical, chemical, thermal, and electrical methods of stimulations were included. The general result of the experiments is the revelation of a remarkable similarity of response in the plant and the animal.

Practical Sanitation. By George Reid, M.D., D.Ph. Seventeenth Edition. London: Charles Griffin and Co., Ltd. 1913.

Although it is only eighteen months since the sixteenth edition of this book was published, progress in sanitation has been so rapid that in the eighteenth edition a good many alterations and additions have been found necessary. The book gives a thoroughly practical outline of the elements of sanitation, and inspectors, builders, and plumbers, medical officers of health, and householders will find it full of valuable information. The appendix on English sanitary law will serve as a useful guide to the reading of candidates for examinations on the subject.

The Application of Physico-chemical Theory to Technical Processes and Manufacturing Methods. By Prof. Dr. R. Kremann. Translated from the German by Harold E. Potts, M.Sc.(Liverpool), and Edited by Albert Mond, Ph.D. London: Constable and Co., Ltd. 1913.

The value of a knowledge of physical chemistry to the enlightened technical chemist who is anxious to keep abreast of the times and to shake himself free from the bondage of rule-of-thumb methods is fully recognised on all sides, and in spite of the difficulty of the subject it is most necessary that the student should get an early acquaintance with it, so that when he approaches more advanced work in his own special branch he should be able to do so from the physico-chemical standpoint. This book gives a useful introduction to the subject. The chapters are graduated in difficulty, and a minimum amount of mathematics is introduced. Many industries are adequately dealt with, and the phase rule is particularly clearly explained and illustrated. The translation has been carefully done and the book is well printed; the only error which a careful examination has brought to light being in the lettering of the diagram of a gas-engine, where the illustration does not agree with the text.

Industrial Research in America. Presidential Address. By Arthur D. Little. Reprinted from the *Journal of Industrial and Engineering Chemistry.* 1913.

This Presidential Address, delivered before the American Chemical Society, gives a very stimulating account of the state of industrial research in America, and contains some remarkable facts and figures concerning the development of certain industries and the solution of some technical problems by American chemists. The research work done by the ten great scientific bureaus organised and controlled by the Department of Agriculture has led to results of great value, some of which are briefly summarised in the address, and short accounts are also given of the pioneer work in industrial research which is being

done by some of the Universities and technical schools. The words of the President regarding the applications of chemical science to the industries in the future are so generally applicable that they are well worth quoting:— "We shall need for years to prosecute a vigorous campaign for a better understanding by the general public of what chemistry is and what research is. The popular imagination is ready to accept any marvel which claims the laboratory as its birthplace, but the man in the works still disbelieves that two and two in chemical nomenclature make four. We need a multiplication of research laboratories in special industries, each with an adequate staff of the best men obtainable and an equipment which gives full range to their abilities."

Die Chemische Verwandtshaft. ("Chemical Affinity"). By Dr. Max Speter. Leipzig: Philipp Reclam, jun. 1913. (80 Pf.).

This booklet deals with the connection between chemical affinity and thermic, electric, and radiant energy, and gives a short summary of the experimental data which have been collected and the general laws which have been deduced from them. The author does not put before his readers many speculations as to the nature of the force which brings about the combination of substances, but confines himself to the statement of the positive results which have been obtained, and considering the very small size of the book he does so with great completeness and clearness.

Whitaker's Almanac for 1914. Half Bound, 904 pages. J. Whitaker and Sons.

A list of some thirty-five new features are given as having been introduced in this issue, enough to show that the publishers are fully determined to maintain the reputation of the almanac. Among the items we note the Home Rule Bill, Royal Flying Corps, Labour Unrest, Aeronautics, National Health Insurance Amendment Act, Wireless Telegraphy, and other current topics. "Whitaker's Almanac" is too well known to require further introduction: we need only say that it is as good as ever.

Whitaker's Peerage, Baronetage, Knightage, and Championage for 1914.

During the past year Honours appear to have been distributed somewhat more sparingly than of late, and the Obituary list is ominously long. A great deal of interesting and useful information is given in the way of footnotes, in addition to the official matter. Amongst other things we note that much of the fable and superstition connected with the Coronation Stone, so well known to all visitors to the Abbey, has been cleared away by Sir Archibald Geikie, who, speaking as a geologist, declares that the stone was almost certainly quarried in the sandstone district between Argyll and the Forth. An interesting account is given of the ceremony of the Coronation of the present King, together with many quaint observances not generally known.

CORRESPONDENCE.

INSTITUTE OF CHEMISTRY CONFERENCE.

To the Editor of the Chemical News.

Sir,—As one who has criticised the ways of the Institute of Chemistry, I am glad to see that there is a decided opinion among teachers of chemistry that this Society might be improved.

I would suggest that it would be in its best interests to abolish the practical examinations altogether. To suggest that any examiners can tell whether a man is a competent chemist by working in a strange laboratory for six hours or so a day for three or four days, under conditions that are never found in practice, seems to me a very unscientific way of finding out a man's capabilities. The exercises set are frequently open to criticism as to whether an analyst could do them in the time allowed, even in one's own laboratory. The large percentage of failures show there must be something wrong.

As an alternative to practical examinations, suppose the Institute insisted upon a two years course of general chemistry in a college, or a three years course at evening classes, and then made each student analyse correctly a series of salts the composition of which was known only to a small examining committee. The diploma not to be given until the series were correctly analysed. This might take two or four or more years, either at a day college or evening classes. I do not mean the same series for every student.

I am sorry to see the attitude taken up by some gentlemen, that class distinctions have anything to do with abilities. There are chemists in this country who have had to make the best use they could of the limited opportunities for learning which they could afford, and whose opinion would now be taken in preference to a F.I.C. in cases of dispute, but if any of these gentlemen applied under the terms of the Charter for election to the Fellowship they would probably be told that "their qualifications are not such as would justify the Council in admitting them to the F.I.C.," and probably, without any disrespect, not one of the Council would be equal to them scientifically in their special branches.—I am, &c.,

Ernest A. Lewis.

310, Dudley Road, Birmingham,
December 20, 1913.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances des l'Académie des Sciences. Vol. clvii., No. 19, November 10, 1913.

Origin of Cyclic Bases of Coal-tar.—L. C. Maillard. —The cyclic bases of tars undoubtedly derive their nitrogen from ancient protein material, and according to the author's view the intermediate products are nitrated humic matter resulting from the condensation of the sugars (constituents of cellulose, &c.) with amino-acids (constituents of proteins). The formation of volatile bases at the expense of the humic matter is due to pyrogenation, but it is certain that the union of the amino-nitrogen with the carbon chain of the sugars occurs before pyrogenation.

Decomposition of Halogen Alkylates of Hexamethylene-tetramine. — Marcel Sommelet. — Boiling water is capable of decomposing the halogen alkylates of hexamethylene-tetramine, particularly those which are derived from benzyl chloride and analogous compounds. The somewhat unexpected result is the formation of the aldehyde of the halogen derivative. The chlorobenzylate is so sensitive to the action of water that benzoic aldehyde is obtained by simply heating its solution in aqueous alcohol. The bromotoluylates of hexamethylene-tetramine are similarly transformed into toluic aldehydes.

MEETINGS FOR THE WEEK.

Monday, 5th.—Society of Chemical Industry, 8. "Viscosity of Oils," by J. L. Strevens. "Oxygen Content of Gases from Roasting Pyrites," by Lewis T. Wright. "Electrical Conductivity of Milk during its Concentration, with suggestions for a Practical Method of Determining the End-point in the Manufacture of Sweetened Condensed Milk," by L. C. Jackson, Leslie McNab, and A. C. H. Rothera. "Monazite from some New Localities," by S. J. Johnstone.

Tuesday, 6th. / Thursday, 8th. { Royal Institution, 3. (Christmas Lectures, adapted to a juvenile auditory). "A Voyage in Space," by Prof. H. H. Turner, D.Sc., F.R.S.,

Wednesday, 7th.—Royal Society of Arts, 5. (Juvenile Lecture. "Electric Vibrations and Wireless Telegraphy)" by R. P. Howgrave-Graham, M.I.E.E.

THE CHEMICAL NEWS.

VOL. CIX., No. 2824.

THE DIMETHYL PHOSPHATES OF THE RARE EARTHS.*

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THE study of methods for the separation of the rare earths and of new compounds of the rare earths that seem likely to be of use for such purposes has for a long time occupied the attention of those interested in this branch of chemistry.

The rare earth salts of dimethyl phosphoric acid seemed, on preliminary investigation, to be possessed of properties which would make dimethyl phosphoric acid an extremely valuable reagent for the separation of some of the rare earths. Therefore a study of the properties of these compounds was commenced.

This investigation involved the preparation of dimethyl phosphoric acid; the preparation of the rare earth compounds from this; the determination of the composition and solubility of these compounds; and, finally, several fractionations of rare earth mixtures.

Preparation of Dimethyl Phosphoric Acid.—This acid was prepared, according to the method of Hugo Schiff (*Chem. Central Blatt*, 1857, 761—763, 864), by allowing methyl alcohol to drop slowly into phosphorus oxychloride. About 200 cc. of phosphorus oxychloride were placed in a litre flask, and 250 cc. of methyl alcohol were added, drop by drop, through a separatory funnel fitted to the flask. During the reaction the flask was shaken in a stream of cold water, and the temperature maintained between 25° and 30°. The large quantities of hydrochloric acid gas and methyl chloride which were evolved passed off through a side tube. At the completion of the reaction, which required from an hour to an hour and a-half, there remained a colourless somewhat syrupy liquid, consisting of both dimethyl phosphoric and phosphoric acids with some hydrochloric acid and methyl chloride. This was removed to an evaporating dish, and heated upon the steam-bath until the hydrochloric acid and methyl chloride were expelled. The syrupy acids were then diluted and neutralised with barium carbonate. The phosphoric acid was removed as barium phosphate. The precipitate was filtered off, leaving a clear filtrate consisting of a solution of barium dimethyl phosphate, together with traces of barium monomethyl phosphate. This solution was treated with just sufficient sulphuric acid to precipitate all the barium as the sulphate, which after digestion at 95° was removed by filtration, leaving a clear solution of dimethyl phosphoric acid.

Yttrium Dimethyl Phosphate.—This salt was obtained by dissolving yttrium hydroxide in dilute dimethyl phosphoric acid. After stirring for some time the liquid became clear. The solution was then filtered and placed upon a water-bath, the temperature of the latter being kept at about 90°. This treatment caused a quantity of crystalline yttrium dimethyl phosphate to form. The precipitate was filtered off and washed with boiling water. The compound was next dissolved in as small an amount of water as possible, and permitted to crystallise by spontaneous evaporation. Groups of white needle-like crystals, radiating from a common centre, were formed. These were removed, dried between filter-papers, and then placed in an oven at 100° for four hours. The results of the analysis seemed to show that a very small amount of water was retained. Further drying at the same temperature failed to make any difference.

Yttrium dimethyl phosphate dissolves in water at 25° to the extent of 2·80 parts of the anhydrous salt to 100 parts of water. At 95° only about 0·55 part dissolve in 100 parts of water.

Y_2O_3; calculated, 24·34; found, 24·06.

Lanthanum Dimethyl Phosphate.—This substance was prepared by dissolving the oxide in dilute dimethyl phosphoric acid. The solution, after filtration, was concentrated upon a water-bath until a skin began to form upon the surface, after which it was permitted to crystallise by spontaneous evaporation. The resulting crystals were dissolved in water and re-crystallised once again by spontaneous evaporation. These crystals were separated from excess of mother-liquor by pressing between filter-papers, and finally dried in air.

Lanthanum dimethyl phosphate forms white hexagonal crystals. One hundred parts of water dissolve 103·7 parts of the anhydrous salt at 25°. The solubility at 100° did not vary like the other rare earths. The solubility at 95° appeared to be somewhat difficult to obtain owing to the fact that the solution had a tendency to become colloidal.

In order to determine the phosphorus a weighed sample of lanthanum dimethyl phosphate was first fused with sodium peroxide to oxidise the methyl groups and get the phosphorus present as phosphate. The usual method was then followed.

Calculated: La_2O_3, 29·63; P_2O, 38·75. Found: La_2O_3, 29·45; P_2O, 38·63.

From the above analysis it was considered that the compound contained 4 molecules of water of crystallisation, as shown by the formula $La_2[(CH_3)_2PO_4]_6 4H_2O$.

Cerous Dimethyl Phosphate.—The cerous compound was obtained by treating cerous carbonate with a dilute solution of the acid. The clear solution was evaporated on the water-bath until a skin began to form upon the surface, as was observed in the case of the preceding substance. It was further concentrated by spontaneous evaporation. The crystals obtained in this manner were again crystallised from water.

Cerous dimethyl phosphate is a white crystalline solid belonging to the hexagonal system. It is very soluble in cold water, but less soluble in hot. One hundred parts of water dissolve 79·6 parts of the anhydrous salt at 25° and about 65 parts at 95°. Upon analysis 33·08 per cent CeO_2 was found. This still remained after drying for some time at 100°, and corresponded to the formula $Ce_2[(CH_3)_2PO_4]_6.H_2O$.

Praseodymium Dimethyl Phosphate.—A solution of this dimethyl phosphate was prepared by dissolving praseodymium oxide in the acid. The liquid was concentrated on the water-bath until small crystals began to form, after which it was set aside to evaporate at ordinary temperatures. The compound purified by re-crystallisation formed green hexagonal crystals. 64·1 parts were dissolved by 100 parts of water at 25°.

Neodymium Dimethyl Phosphate was prepared in a similar manner to the praseodymium compound. It forms pale lilac coloured hexagonal plates. At 25°, 56·1 parts dissolve in 100 parts of water, while at 95° only about 22·3 parts are dissolved by 100 parts of water. An analysis showed the presence of 32·27 per cent of Nd_2O_3, thus pointing to the formula $Nd_2[(CH_3)_2PO_4]_6$.

Samarium Dimethyl Phosphate.—A small quantity of the acid was neutralised with samarium oxide. The solution thus obtained was concentrated on the water-bath until nearly solid, owing to the formation of the dimethyl phosphate crystals. It was filtered while still hot. The salt was dissolved in water and crystallised by evaporation at ordinary room temperature.

Samarium dimethyl phosphate forms cream coloured hexagonal prisms. One hundred parts of water dissolve 35·2 parts of the salt at 25° and about 10·8 parts at 95°. 33·11 per cent Sm_2O_3 was found to be present, indicating no water of crystallisation like most of the rare earth dimethyl phosphates.

* Contribution from the Chemical Laboratories of New Hampshire College.

Gadolinium Dimethyl Phosphate was separated from its solution by carefully heating.

It forms white needle-like crystals very similar to the yttrium compound. One hundred parts of water dissolve 23·0 parts of the salt at 25°, while only 6·7 parts are dissolved by the same quantity at about 95°. The compound contained 34·00 per cent Gd_2O_3.

Erbium Dimethyl Phosphate was prepared in a similar way to the ytterbium salt described below.

It forms very pale coloured needles, 1·78 parts dissolving in 100 parts of water at 25°.

Ytterbium Dimethyl Phosphate.—The ytterbium oxide was dissolved in a slight excess of hydrochloric acid and the solution diluted considerably. A sufficient quantity of dimethyl phosphoric acid to react with the ytterbium present was neutralised with sodium carbonate, and then made slightly acid with a few drops of dimethyl phosphoric acid. This solution was diluted and slowly added to the ytterbium chloride with careful stirring. A precipitate of ytterbium dimethyl phosphate formed, which slightly increased in amount on heating the solution to 100°. The precipitate was filtered off, dissolved in cold water, and again precipitated by heating. The white needle-like crystals dissolve to the extent of 1·2 parts per 100 parts of water at 25°. Only 0·25 are dissolved by 100 parts of water at about 95°. An analysis showed 35·73 per cent Yb_2O_3, which corresponds to the amount contained in the formula of the anhydrous substance.

Table of Solubilities of Dimethyl Phosphates.

Element.	Crystal form.	Parts of salt per 100 parts of water at 25°.
Lanthanum	Hexagonal crystals	103·7
Cerium	„ plates	79·6
Praseodymium	„ „	64·1
Neodymium	„ „	56·1
Samarium	„ prisms	35·2
Gadolinium	Long needles	23·0
Yttrium	„	2·8
Erbium	„	1·78
Ytterbium	„	1·2

Fractionation of Material.—Since, as already stated, the study of new compounds of the rare earths is carried on mainly to obtain compounds adaptable to a more complete and more rapid separation of these elements, no study would be complete without determining the behaviour of mixtures of the dimethyl phosphates. Several fractionations were conducted, and the method employed was that of precipitation by heat, in the case of the less soluble compounds a dilute solution was prepared. The beaker containing this solution was then placed in a water-bath and the temperature of the bath gradually raised, the solution being constantly stirred. As soon as a fair amount of precipitate had formed, the liquid was filtered off and the precipitate retained as fraction I. The filtrate was again heated until another lot had separated and again filtered. The dimethyl phosphates collected from this second heating were put aside as fraction II. In this manner fractions were taken up to and inclusive of 95°. Additional fractions were obtained by fractionally evaporating the mother-liquor.

These fractions were further fractionated by dissolving the least soluble fraction in water, and heating in the water-bath to the temperature at which fraction I. was removed. The precipitate which had formed at this point was removed by filtration and retained as fractions I.—II. The filtrate was used to dissolve fraction II., and the solution heated as before to the temperature of removal of fraction II. The precipitate was taken as fraction II.—2, and the filtrate used to dissolve fraction III. By proceeding in this manner any degree of fractionation which was desired could be obtained.

During and at the completion of the fractionation various fractions were examined with regard to colour of oxide, nitric acid solution, and spectrum.

Gadolinium Material.—A material containing gadolinium with only sufficient traces of terbium to colour the oxide orange-brown was first submitted to fractionation with dimethyl phosphoric acid.

The oxide of this crude gadolinium was dissolved by stirring with the acid until all had dissolved. The liquid was then treated as described above.

The fractions were taken as follows:—Fractions I., I.—2, I.—3 at 65°; fractions II., II.—2, II.—3, at 90°; fractions III., III.—2, III.—3, after evaporating the mother-liquor from fractions II. to one-half volume; and fractions IV., IV.—2, IV.—3 upon complete evaporation.

A fair idea can be formed with regard to the rapidity of the method by observing the change in colour of the oxides. The oxide from fraction II. was of a dark brown colour; that of fraction IV. light brown, and that of fraction IV.—3 pale cream.

This showed a rapid concentration of the gadolinium in the most soluble fractions, while the impurity—terbium—collected in the least soluble.

It is interesting to note that this fractionation required only about forty-eight hours to give a comparatively pure gadolinium. This shows a great increase in the rapidity of the separation over all previous methods.

Fractionation of Yttrium Material.—The next oxides consisted of a mixture of those of yttrium, holmium, and dysprosium with traces of erbium, samarium, gadolinium, terbium, neodymium, and praseodymium. They were dissolved in hydrochloric acid, the solution diluted and boiled with an excess of sodium hydroxide. The precipitated hydroxides were filtered off, washed with hot water until free from chlorides, and dissolved by stirring with the dilute dimethyl phosphoric acid. The resulting solution was then submitted to the usual fractionation.

Fraction I. was removed at 38°, fraction II. at 48°, fraction III. at 65°; fraction IV. at 96°, while fractions V., VI., VII., and VIII. were taken by fractionally evaporating the mother-liquor from fraction IV.

Fraction I.—The oxide was yellowish, and the absorption spectrum showed a rapid concentration of erbium. Holmium and dysprosium were also present.

Fraction II.—This portion gave a yellowish coloured oxide. The spectroscope showed holmium and dysprosium with very small quantities of erbium.

Fraction VI.—The oxide was coloured an orange-brown. An intense absorption proved the presence of very much dysprosium, less holmium, and the merest possible trace of neodymium.

Fraction VII.—Reddish brown oxide. The absorption spectrum was very weak, showing the presence of a small amount of neodymium and traces of samarium and dysprosium. The green band of holmium could barely be detected.

Fraction VIII.—This gave an orange-brown oxide. The spectrum showed intense absorption bands, indicating the presence of a large quantity of neodymium, a very little praseodymium, and only a trace of samarium.

Fractionation of a mixture of earths, from monazite, giving more soluble double sulphates. The earths present consisted largely of gadolinium and dysprosium with small amounts of terbium, holmium, and neodymium.

The oxides were warmed with dimethyl phosphoric acid until entirely converted into dimethyl phosphates, after which the thick mass was stirred with water until dissolved.

The fractions were collected as follows:—Fractions I. to III. up to 95°; and fractions IV. and V. by evaporation of the mother-liquor from fraction III.

Fraction I. gave a brownish yellow oxide, which, when dissolved in nitric acid, gave a yellowish green solution. With the aid of the spectroscope it was found that large amounts of dysprosium were present, accompanied by a little holmium.

Fraction II.—The oxide was chocolate-brown. Its nitrate solution was faintly green and showed weak absorption bands of dysprosium and terbium.

Fraction V.—Oxide red-brown. Absorption spectrum

indicated very small quantities of neodymium and dysprosium.

It will be observed from the above fractionations that the rate of separation of the rare earths is vastly greater than practically all the methods given up to the present time. Lanthanum, cerium, praseodymium, neodymium are left at once in the mother-liquor. Samarium, europium, and gadolinium are much less soluble than those previously mentioned, while they are more soluble than terbium, dysprosium, and holmium. Erbium, thulium, yttrium, ytterbium, &c., collect in the least soluble portions.

Since the solubilities of these compounds are the reverse of the usual type, they may be used for the rapid purification of many of the rare earths. For instance, we can easily remove traces of neodymium from samarium by this means, as the samarium dimethyl phosphate separates before the neodymium compound.

It is necessary to state that there is some inconvenience when working with the salts of dimethyl phosphoric acid, since they undergo gradual decomposition. A gelatinous precipitate is formed very slowly in the case of the rare earths, which filters with difficulty.

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REVIEW AND INTERPRETATION OF RECENT EXPERIMENTS WHICH EXTEND AND ELUCIDATE THE DOMAIN OF THE PASSIVITY OF METALS.*

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(Concluded from p. 4).

5. *First Theory.*

THE first theory was proposed at a time (1910—11) when the experiments of Le Blanc concerning the chemical polarisation of active metal electrodes were already known, and when the palladium-zinc experiments were made in order to clear the matter up; the other experiments mentioned above were not yet known, however. The theory, therefore, aimed at devising a mechanism which would admit of chemical polarisation without denying the possibility that a system, and a passive metal-anode likewise, might primarily emit anodic ions. I should like to emphasise at this place already that this question is more satisfactorily answered by this first theory than by the second one.

The first theory conceives a mechanism of the chemical polarisation after the type of the Pd-Zn electrode (Reichinstein, *Zeit. Elektrochem.*, 1911, xvii., 699). The rate of formation of the Pd-H alloy in the cathodic polarisation of the $Pd\text{-}H_2SO_4$ electrode is given by the momentary concentration of the Pd and H atoms near the boundary of the solid electrode and of the liquid electrolyte. Let us now assume that the contact with the electrolyte at the boundary electrode/electrolyte is not formed by the solid metal, but by a solution (= alloy) of all those substances whose ions are represented in the electrolyte. The volume which this hypothetical alloy occupies in the electrode is designated the *electrode volume.*

When we add to the electrolyte of the $Pd\text{-}H_2\text{-}H_2SO_4$ electrode some Zn salt, some zinc will be deposited in the electrode volume already at open circuit, because the thermodynamical equilibrium demands that the potentials $H_2H^{\cdot}$ ion and $Zn\text{-}Zn^{\cdot\cdot}$ ion must finally be equal to one another.

We now make the assumption that the zinc entering the electrode volume diminishes the concentration of the Pd atoms there. When we now treat the electrode cathodically, the rate of formation of the Pd-H alloy will be smaller, and the polarisation will be greater, than before. As a consequence some more zinc will be deposited on the electrode in accordance with the higher potential. The formation of the Pd-H alloy will proceed more slowly, and the polarisation will finally rise so high that zinc alone is deposited.

Analogously a Cu electrode has a certain oxygen concentration in the electrode volume already before the current is turned on. The potentials of the systems $Cu\text{-}Cu^{\cdot\cdot}$ ions and OH' ions always remain equal to one another, with or without the current flowing. That may be supposed to become possible by the splitting of the electric current into two components: two primary processes are *simultaneously* taking place at the anode—

$$(1)\quad Cu + 2F(+) \longrightarrow Cu^{\cdot\cdot}.$$
$$(2)\quad OH' + 1F(+) \longrightarrow OH.$$

Whilst the first process depresses the concentration of the Cu atoms in the electrode volume, the second process raises the O concentration there, and it is therefore the electric current which maintains the equilibrium in the electrode volume. Both the reactions increase the polarisation, and the purely chemical compensation processes oppose them. The process which is subject to chemical inertia is the oxidation of the massive copper by the aid of the oxygen in the electrode volume in the presence of the $H^{\cdot}$ ions of the electrolyte (any reaction between the oxygen of the electrode volume and the Cu atoms present in it is excluded, because there is equilibrium between the two systems, which, as we shall see, is a weak point of the first theory). When under special conditions the described oxidation takes place at a slow rate, the O concentration in the electrode volume and consequently the polarisation rise to a high degree, until finally another compensation process sets in, for example, O_2 generation (= passivity). The equations of this theory may be deduced as follows:—

Let there be: P_1, the electrolytic solution tension of the oxygen concentration in the alloy metal-oxygen, P_2 the electrolytic solution tension of its metal concentration, and p_1 and p_2 the corresponding concentrations of the ions in the electrolyte, which are assumed to be very high (= constant, practically not variable by small current densities). When the system tends to equilibrium, only P_1 and P_2 will change, and the conditions of equilibrium will be—

$$\frac{RT}{n_1F}\ln\frac{P_1}{p_1} + \frac{RT}{n_2F}\ln\frac{P_2}{p_2} = 0 \quad . \quad . \quad . \quad (1)$$

or—

$$\sqrt[n_1]{\frac{P_1}{p_1}} = \sqrt[n_1]{\frac{p_2}{P_2}} \quad . \quad . \quad . \quad (2)$$

In the most simple case where the chemical valencies n_1 and n_2 are equal we shall have—

$$P_1P_2 = p_1p_2 = K \quad . \quad . \quad . \quad (3)$$

where K is a constant. When we bear in mind that according to our assumption there is always (current flowing or not) equilibrium between the systems oxygen-oxygen ions and metal-metal ions, we may interpret equation (3) to mean that, when the solution tension of the metal decreases as the current flows because its concentration in the alloy is reduced, the solution tension of the oxygen must decrease at the same time. We therefore write—

$$\delta P_1 . P_2) = 0 \quad . \quad . \quad . \quad (4)$$

By differentiating (4) we obtain—

$$\frac{\delta P_1}{P_1} + \frac{\delta P_2}{P_2} = 0$$

$$-\frac{\delta P_1}{P_2} = \frac{P_1}{P_2} \quad . \quad . \quad . \quad (5)$$

If we now send the quantity of electricity 1 in the direction electrode-electrolyte, the system $O\text{-}OH'$ will transport the fraction r of the quantity of electricity which will discharge OH' ions and enrich the alloy in oxygen, whilst the electricity quantity $(1 - r)$ will diminish the

* "A Contribution to the General Discussion on "The Passivity of Metals" held before the Faraday Society, November 12, 1913. Translated from the German.)

metal concentration in the alloy. The relation between these two quantities is the following:—Let the potential of the alloy with regard to the electrolyte be π during a short interval, while the current is flowing. The work to be done in order to transport the quantity of electricity 1 from the electrode to the electrolyte will be—

$$\pi = r\frac{RT}{n_1F} ln \frac{P_1}{p_1} - (1-r)\frac{RT}{n_2F} ln \frac{P_2}{p_2} \quad . \quad (6)$$

The ratio of the increase in the oxygen concentration to the decrease in the metal concentration of the metal-oxygen alloy may be considered equal to the ratio of these two quantities of electricity; hence—

$$-\frac{\delta P_1}{\delta P_2} = \frac{r}{1-r} = \frac{P_1}{P_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

and consequently—

$$r = \frac{P_1}{P_1+P_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

By combining (8) with (3) we find—

$$r = \frac{K}{K+P_2{}^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Or in words: *When with the anodic treatment of a metal its concentration in the metal-oxygen alloy becomes small, then the system O-OH' will effect the whole transport of electricity: r therefore becomes equal 1. The electrode now transports the electric current in a way as if it were a highly noble metal; its capability of primarily forming ions is completely suppressed, and it is limited to a secondary formation of ions.*

Let us further assume that the total current in the anodic treatment of a copper electrode in the presence of H· and of Cu·· ions of high concentration be given by the reaction—

$$2OH' + 2\oplus \rightarrow H_2O + O.$$

We will also suppose that the slow process of chemical compensation is defined by—

$$Cu + 2H^{\cdot} + O \rightarrow Cu^{\cdot\cdot} + H_2O.$$

Let this process be much slower than the replenishing of the OH' ions which are consumed by the current. And finally let the experimental conditions be such that the rate of percentage rise in the Cu ion concentration at the electrode within the time t is so small that it may be neglected.

If, then—

x be the total oxygen concentration which the current has supplied up to the moment t;

x_1 that concentration of the oxygen which has chemically been bound up to the moment t by Cu and H· ions;

$c = x - x_1$ the oxygen concentration on the electrode surface at the moment t;

k_0 the velocity coefficient of the reaction:

$$Cu + 2H^{\cdot} + O \rightarrow Cu^{\cdot\cdot} + H_2O.$$

i_t a variable current intensity for which the same direction is, however, always maintained;

and if, as stated, the oxygen concentration on the electrode surface at the moment t be—

$$c = x - x_1. \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

then the concentration at the moment $(t+dt)$ will be—

$$c + dc = x + dx - (x_1 + dx_1) \quad . \quad . \quad . \quad (11)$$

According to Faraday's law

$$dx = ki_{(t)}dt \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

where k is a proportionality factor.

The velocity of the reaction—

$$Cu + 2H^{\cdot} + O \rightarrow Cu^{\cdot\cdot} + H_2O$$

$\left(\frac{dx_1}{dt}\right)$ is at any moment proportional only to the actual oxygen concentration because the concentration of the metallic copper is *eo ipso* constant, and the concentration of the H· ions constant by hypothesis, and we obtain finally—

$$dc = (ki_{(t)} - k_0 c)dt \quad . \quad . \quad . \quad . \quad . \quad (13)$$

from which we find—

$$c = e^{-k_0 t}\left(C_1 + \int_0^t e^{k_0 t} ki_{(t)}dt\right) \quad . \quad . \quad . \quad . \quad (14)$$

where C_1 is the integration constant. From the initial condition (for which $t=0$) we see at once that the integration constant is dependent only upon that oxygen concentration which corresponds to the electrode when no current is flowing. This value of c is in our case given by the equilibrium potential of the copper electrode. If we now consider that the chemical polarisation of a type of electrode such as we deal with in the copper electrode will, at small current density already, assume relatively large values, which differ strongly from the equilibrium potential of the base electrode, C_1 may be regarded as infinitely small with respect to the c values, and the equation may be written in the form—

$$c = ke^{-k_0 t}\int_0^t e^{k_0 t} i_{(t)}dt \quad . \quad . \quad . \quad . \quad . \quad (15)$$

This theory, which very satisfactorily characterises the chemical polarisation on condition that all the metals become primarily active as anodes, fails in many instances. Without entering into detail I will emphasise the consideration which will help us on to the right way.

We have seen that in the consideration of the anodic treatment of a metal the theory leads to quasi-secondary formation of ions, although in principle the theory starts from primary anodic formation of ions. That is just the desired result of the theory. This result is not arrived at, however, when we attempt to explain the cathodic chemical polarisation by the aid of this theory. For if we imagine that the two chief components of the electrode volume consist, in the cathodic polarisation of the Cu-CuSO$_4$ electrode, of Cu and of H atoms, then their quotient is constant, not their product, and the increase in the concentration of the one calls forth a simultaneous increase in the concentration of the other.

Further—and that is the chief drawback of the theory—we cannot, with its aid, come to the above-mentioned type of two reactions, of which the one is retarded by a rise in the O concentration whilst the second increases its velocity in a regular manner. This type of two reactions, we have recognised, can alone elucidate the phenomena of passivity. We can easily comprehend that we shall arrive at such a type of reaction if we imagine some reaction to take place within the electrode volume, *i.e.*, between its constituents. The first theory does not admit of that, because there is always equilibrium within the electrode volume; and all the compensation processes of which the first theory admits are indirect reactions. In order, therefore, that we may imagine a larger number of possible compensation processes, the mechanism of the electrode volume should be so designed that there should not prevail equilibrium in it while the current is flowing. The entire current must be transported by *one* system from the electrode to the electrolyte.

We also saw that the prototype of the mechanism of chemical polarisation, the Pd-Zn experiment, renders it necessary to ascribe to the zinc which enters the electrode volume a diminution of the concentration of the Pd atoms. How is this to happen? This effect is difficult to conceive if we regard the electrode volume as constant, and if we make no new hypothesis as to the mutual influences of the various constituents of the electrode volume. The simplest assumption which at once enables us to describe all the experiments mentioned is this: *The sum of the concentrations of all the constituents of the electrode volume is always constant, whether the current flows or not.*

6. *The Constant-Sum Hypothesis and the Second Theory.*

(Reichenstein, *Zeit. Elektrochem*, 1913, xix., 672).

We presume that the electrode volume is always fully saturated, and that any new constituent, possibly introduced by the electric current, ejects part of the old substances.

For the present I am not in a position to maintain the idea of a primary activity of all the systems. In view, however, of the fact that this theory satisfactorily answers all the questions concerning the chemical polarisation, as well as those concerning the spontaneous solution of solid bodies in the presence of oxidising agents, we may for the present rest satisfied with the assumption that in aqueous solutions the transport of the electric current across the boundary electrode/electrolyte is effected only by the OH' and the H· ions.

When a metal electrode is treated anodically the oxygen introduced pushes the metal atoms out of the electrode volume—the same will happen on the cathode by the H_2 introduced—and the chemical equilibrium prevailing before the current was flowing will be destroyed. The oxygen now begins to react with the metal atoms of the electrode volume. Let this reaction be of the form—

$$Me \mid O + 2H^{\cdot} \rightarrow Me^{\cdot\cdot} + H_2O,$$

where Me and O are respectively an atom of the metal and of the oxygen of the hypothetical alloy, and H· concerns the electrolyte.

If the concentrations of the three substances reacting with one another are x, y, z, the velocity of the compensation process can be formulated as follows:—

According to the hypothesis of the constant sum

$$x + y = a \quad . \quad . \quad . \quad . \quad (16)$$

where a is a constant; the velocity v

$$v = k_0 z^2 xy = k_0 z^2 y(a - y) \quad . \quad . \quad (17)$$

when, in a special case, z is a constant, the $(v - y)$ curve has a maximum. Now—

$$v = k'(ay - y^2) \quad . \quad . \quad . \quad . \quad . \quad (18)$$

from which

$$\frac{dv}{dy} = ak' - 2k'y$$

and

$$\frac{d^2v}{dy^2} = -2k'.$$

The maximum corresponds to the value $y = \frac{a}{2}$.

When with a certain current density of the electrolysis the compensation process is so rapid that the oxygen concentration of the electrode volume does not rise above the value $\frac{a}{2}$ (which we may call the *critical concentration*), then there will be no reason to fear that another compensation process will set in, *e.g.*, generation of oxygen (=passivity). When, however, the critical concentration is exceeded, the compensation process will necessarily be retarded, and the O concentration will increase rapidly until a new compensation process sets in. Instead of the above-mentioned equation of the first theory, which defines the accumulation of the O concentration in the electrode volume after closing the circuit:—

$$\frac{dy}{dt} = ki - k_0 y,$$

where i is the current intensity of the continuous current, we have now—

$$\frac{dy}{dt} = ki - v \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

and by combining (19) and (18)—

$$\frac{dy}{dt} = ki - k'ay + k'y^2 \quad . \quad . \quad . \quad (20)$$

This equation gives us the above-discussed point of inflection for the y—t curve, that is to say, also for the curve which illustrates the rise of the polarisation with time after closing the circuit.

We have now arrived at some point of reference enabling us to describe the experiments of Andrejew.

When we immerse a foil of gold in a solution of KCN which contains an oxidising agent like O_2, H_2O_2, or O_3 in solution, two purely chemical reactions will come into play:—

I. The formation of the gold-oxygen alloy.

This process is missing in the electrolytic dissolution of metals because in their instance the oxygen is directly supplied by the primary discharge of OH' ions, whilst here the oxygen is supplied by a chemical reaction (= decomposition of the oxidising agent). If the oxygen were not to disappear owing to the dissolution of the gold, we should finally arrive at an equilibrium between its concentration in the electrode volume and the concentration of the oxidising agent in the aqueous KCN solution. We may suppose that in one and the same oxidising agent these two concentrations will bear a rectilinear relation. Now the formation of the gold-oxygen alloy, we shall see, does not proceed at an infinitely rapid rate, yet not so slowly that this process should become decisive for the entire process of solving the gold. The CN' ions are, moreover, not in contact now with the compact gold metal, but in contact with the gold-oxygen alloy, and process II. is taking place.

II. $2Au \mid O\,(\text{alloy}) + H_2O + CN' \rightarrow 2Au(CN)'_2 + 2OH'$.

This process may, of course, proceed in several stages. When we increase the O concentration of the alloy by increasing the concentration of the oxidising agent in the liquid phase, the critical O concentration will finally be exceeded, and the velocity of the process II. will diminish more and more.

It should here be emphasised that there are many instances in which the rate of oxidation becomes smaller as the oxygen concentration is raised; I will content myself with drawing attention to the table of these cases compiled by van 't Hoff ("Vorlesungen über theoretische und physikalische Chemie," No. 1, Braunschweig, 1898, 238).

The critical O concentration has now been exceeded, and, in accordance with what has been explained, a new chemical process (a second compensation process) must come into play. Such processes are the following: formation of H_2O_2 (observed by Bodländer), formation of gold peroxide.

We recognise that the occurrence of oxide layers must not be regarded as the cause of the delay in the solution of gold. The peroxide films are merely a concomitant feature, which indeed indicates that the O concentration of the alloy has attained high values, but which must by no means be represented as the cause of the dissolution of gold. It is a symptom, like the rise of temperature in the diseased human body.

It is interesting to note that some investigators regard as cause of the passivity that in which other investigators see the consequence of the cause of passivity.

Thus, process I. supplies oxygen to the alloy metal-oxygen, and temporarily increases its concentration, whilst process II. tends to diminish this concentration. In the stationary condition, when the reactions proceed at a constant rate, the concentration of the oxygen in the alloy is dependent upon the two processes I. and II.; that is to say, the O concentration may be increased, not only by increasing the rate of process I., but also by diminishing the rate of process II. *Ceteris paribus*, therefore, the "critical O concentration" (in the process of dissolving gold in diluted KCN) may be exceeded with the aid of oxidation potentials of the oxidising agents, which are so low that they would be ineffective at higher CN' ion concentration. This is in agreement with the experiments of Andrejew, according to which the characteristic film of gold peroxide appears in solutions of KCN ranging from 0·01 to 0·05 per cent, already when air acts as oxidising

agent, which demonstrates that process I. is absolutely necessary. We may draw a comparison as to the spontaneous solution of passive and of active metals in the presence of oxidising agents from this point of view. What could we predict as regards the spontaneous solution of copper and nickel in H_2SO_4 in the presence of oxidising agents? We know that the latter of these two metals belongs to the so-called passive metals, *i.e.*, that the process of solution is slow. We should then expect, from what has been explained, that the critical O concentration of the nickel-oxygen alloy, and hence the retardation in the rate of solution of nickel, will, *ceteris paribus*, always occur at such oxidation potentials of the oxidising agent at which this will not be attainable in the case of copper; and it is altogether doubtful whether the v maximum will experimentally be realised in the dissolution of copper.

Of especial interest from the standpoint of the new theory are the exposition of the cases of the palladium-zinc cathode and the behaviour of the alloys mentioned on the anode.

When a palladium electrode, to the electrolyte of which a zinc salt has been added, is treated cathodically, the current is carried by the H ions. Owing to the prevailing conditions of equilibrium, some zinc will enter the electrode volume and will push out some palladium, already before the circuit is established. When the current flows, the zinc acts as ballast, because it depresses the Pd concentration according to the hypothesis of the constant sum, and hence retards the rate of the compensation process. When the concentration of the zinc in the electrode volume is γ and the sum-constant is a, the maximum of the curve, which expresses the rate of the compensation process (Pd + H reaction) as a function of the H concentration, will correspond, not to the H value, $\frac{a}{2}$, but to $\frac{a-\gamma}{2}$. Now, hydrogen accumulates more and more in the electrode volume, and the polarisation rises. It should be noted that the whole conception forces us to assume a chemical reaction between the H atoms and those Pd atoms which fill up the electrode volume—an assumption which was impossible according to the first theory of there being always equilibrium in the electrode volume. Thus quite generally, any foreign substance entering into the electrode volume which will not take part in the compensation process may be regarded as ballast.

A special interest attaches, from this point of view, to the behaviour of the real alloys forming on the anode. When, in the case of a purely active metal, the maximum of the curve O concentration/velocity cannot be attained, that maximum can, in the case of an alloy as described, be realised, owing to the ballast, at relatively low current density, and the curve will show an inflection. An alloyed anode, therefore, displays formally the properties of a passive metal. We may imagine the whole anodic process on the following lines. As regards the space distribution the electrode, at the beginning of the anodic treatment, has the appearance: *Electrolyte/hypothetical alloy/real alloy/compact base metal.* The anodic treatment carries oxygen into the hypothetical alloy, where it partly displaces both the metals, and the chemical reaction between the oxygen and the base metal sets in. (As a matter of fact the two metals enter into competition with regard to the oxygen; practically, however, the oxygen reacts with the less noble metal only.) The base metal, which has disappeared owing to the chemical reaction, is being replaced in the hypothetical alloy by both the metals of the real alloy. In which ratio? That depends upon the rate of diffusion of the base metal, or upon the rate of the alloy formation of the two metals. If this rate be small, then the concentration of the base metals in the hypothetical alloy (when the current is flowing) will also be small—the velocity of the compensation process will decrease, the polarisation will rise, and finally will follow the decomposition of the real alloy; the electrode then will have the following spatial distribution: *Electrolyte/hypothetical alloy/thin layer of the noble metal/compact base metal.* The noble metal may then separate from the electrode. For this end, we know from galvanoplastic processes, a trace of impurity between the two metals will be sufficient.

In order to keep the rate of alloy formation alluded to small, we must, as has been pointed out already, exercise the greatest care as to the purity of the two metals in building up the real alloy. Certain foreign substances accelerate the alloy formation; nitric acid in particular should here be mentioned; it plays the part of the soldering liquid in soldering two metals.

THE SCIENTIFIC WEEK.

(From Our Own Paris Correspondent).

The Reddening of Leaves.

Prof. Gaston Bonnier has presented to the Academy of Sciences a new study of M. Raoul Combes, concerning the crystallisable substances that are found in leaves. One of these substances of a yellow colour is found in green leaves; it is this substance which produce the reddening of leaves in autumn. M. Combes, who had obtained outside the organism the synthesis of the red substance, by starting from the yellow substance by reduction, has just obtained the inverse, that is to say, the synthetic production of the yellow substance, by starting from the red substance, by oxidation. Thus the general question, the answer to which has been so long sought after in vegetable physiology, has at last been solved. Besides its general importance in the life of plants it is easily understood that this solution may be susceptible of practicable applications, notably in what concerns the different varieties of vines.

The Origin of Petroleum.

Learned men are not agreed as to the origin of petroleum. Two schools exist; one of which attributes the formation of petroleum to the igneous action of carbides on water; the other school considers that the petroleums proceed from a distillation of vegetable origin. Prof. Armand Gautier, following on the recent studies of MM. Aimé Pictet and Maurice Bouvier, which he has made known to the Academy of Sciences, gives the preference to the second hypothesis of a vegetable formation. The two learned Geneva gentlemen have distilled ordinary coal at a pretty low temperature, somewhere about 450° in vacuum. They have thus obtained a special kind of tar vacuum, tar without any phenol or any aromatic hydro-carbides. Washed with alkali and sulphuric acid this vacuum tar treated by sodium gives a powdery product having a discharge of hydrogen. This body dissolved in water gives birth to semi-aromatic alcohols, derived from camphor and from hydrocarbides, having the formula $C_{10}H_{20}$ or $C_{12}H_{22}$, which have the same characteristics as the Canadian petroleums, the same point of fusion, same smell, &c. These are quite new experiments and of the greatest interest.

The Spring Finders.

At the time of the famous experiments undertaken at the second Congress of experimental psychology by the spring finders and adepts of the divining rod, M. Armand Viré, Professor at the Natural History Museum, was exceedingly incredulous. However, he became converted, and indeed became a spring finder himself, and, as it were, in spite of himself. And it must be admitted that his conversion caused some astonishment. During the summer months he invited several spring finders to the grottoes of Padriac, with which he is specially well acquainted and of which the plans have not been published. There were several negative experiments. But two or three spring finders were remarkably successful. On the surface of the soil they followed several subterranean water springs and

arrived at the points where they left the earth and appeared on the surface. These points were previously unknown by the spring finders. M. Edmond Perrier, when presenting these experiments to the Academy of Sciences, added that neither he nor M. Armand Viré take upon themselves the responsibility of these observations. They offer no explanations, but simply give the mere facts.

THE MAP OF THE WORLD TO A SCALE OF ONE MILLIONTH.

M. Charles Lallemand, Director of the Service and Organisation of the General Levelling of France, has given some information concerning the last conference of the international map of a millionth scale. At the first conference, which was held at London in 1909, only seventeen countries were represented. At the present time thirty-one states have joined the convention. M. Lallemand also announced that the Prince of Monaco was taking upon himself the expense of several oceanic pages.

MICROBIAN LIFE.

Microbian cultures are often very difficult. M. Adrien Lucet, Member of the Academy of Medicine, has just shown that a regular agitation or shaking of the liquid mediums used in bacteriology, contrary to the opinion that is generally admitted, acts favourably on these infinitely little creatures. By making these bouillons undergo a slow and continuous movement he has, in fact, been able to obtain cultures as many as eight times more abundant of the microbes of cholera, typhus fever, carbuncle, diphtheria, the glanders, dysentery, and even of lock-jaw, the microbe of which can only be cultivated without the penetration of any air. It was M. Chauveau who communicated M. Lucet's study to the Academy.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, November 20th, 1913.

Prof. W. H. PERKIN, LL.D., F.R.S., President, in the Chair.

MESSRS. R. E. Slade and S. C. Sastry were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Albert Frederick Calvert Royston, Eton Avenue, N.W.; Behari Lal Das, 107/2/1, Manaharpukur Road, Kalighah, Calcutta; Eric Russell Harrap, Maisemore, Ebury Road, Rickmansworth, Herts; Oswald Ryle Horwood, M.A., M.R.C.S., L.R.C.P., Tunstall Rectory, Suffolk; Dan Ivor James, M.A., B Sc., Frondeg, Llandilo, Carmarthenshire; Alexander Williamson McLaren, 3, Hayfield Terrace, Langside, Glasgow; Harold Edwin Temple, 239, Cashel Street, Christchurch, New Zealand; Robert James Wright, M.A., care of R. Burnett, Esq., 336, Pollokshaws Road, Glasgow.

A Certificate has been authorised by the Council for presentation to ballot under By-law I.(3) in favour of Mr. Bertie Mandel Welsh, 80, Hunter Street, Sydney, N.S.W.

The PRESIDENT announced:—1. That the bust of the Rt. Hon. Sir Henry Roscoe which was exhibited at the meeting had been presented to the Society by the friends and former students of Sir Henry Roscoe.

2. That by request of the Council Messrs. Vieweg and Sohn have offered to sell the first volume of the "Literatur Register," by R. Stelzner, to Fellows of the Chemical Society at the reduced price of £3 10s. (original price £4 4s.), provided that not less than twenty copies are sold to Fellows of the Society. Those Fellows who desire to obtain a copy of the "Literatur Register" on these terms are requested to send in their names to the Honorary Secretaries.

The PRESIDENT referred to the meeting of the International Association of Chemical Societies which had been held in Brussels during September, 1913, and drew the attention of Fellows to the abbreviated report of the meeting which the Council have ordered to be printed in the *Proceedings.*

Of the following papers, those marked * were read:—

*286. "*Investigations on the Dependence of Rotatory Power on Chemical Constitution. Part V. The Simpler Esters of the Carbinols,* $CH_3{\cdot}CH(OH){\cdot}R$." By ROBERT HOWSON PICKARD and JOSEPH KENYON.

The following homologous series of esters of normal aliphatic acids have been prepared and examined polarimetrically under various conditions:—(i.) The *esters* of *d*-methylethylcarbinol; (ii.) the *esters* of *d*-methyl-*n*-propylcarbinol; (iii.) the *esters* of *d*-methyl-*n*-butylcarbinol (iv.) the *esters* of *d*-methyl-*n*-amylcarbinol; (v.) the esters of *d*-methyl-*n*-hexylcarbinol; (vi.) the *esters* of *d*-methyl-*n*-nonylcarbinol [these six series range from the acetates to the stearates]; (vii.) the *acetates* and (viii.) the *n*-*dodecoates* of the *d*-carbinols [methylethylcarbinol to methyl-*n*-undecylcarbinol].

Many of these esters (all of very simple constitution) exhibit anomalous dispersion when examined polarimetrically at temperatures above 150° or at various concentrations in solvents such as pyridine, benzene, or carbon disulphide.

*287. "*Co ordination of Rotatory Powers for different Wave-lengths, Temperatures, and Solutions.*" (Preliminary Note). By ROBERT HOWSON PICKARD and JOSEPH KENYON.

The authors have already described the synthesis of thirty optically active carbinols of the general formula $R^1{\cdot}CH(OH){\cdot}R^2$, and some seventy esters derived from some of them. These compounds have been examined polarimetrically for three wave lengths (*a*) in the homogeneous state at different temperatures, and (*b*) in several solvents at various concentrations. It was found (see preceding paper) that many of these under certain conditions exhibited anomalous optically rotatory dispersion.

The attention of the present authors was therefore directed to a paper by H. E. Armstrong and E. E. Walker entitled "The Causes of Variation in the Optical Rotatory Power of Organic Compounds and of Anomalous Rotatory Dispersive Power" (*Proc. Roy. Soc.*, 1913, A, lxxxviii., 388). In this paper it is suggested that anomalous dispersion is caused by the presence of two substances (in the actual cases considered of two isodynamic forms) having rotatory powers of opposite sign and different dispersive powers.

In the case of esters of such simple constitution as those described in the preceding paper, the suggested explanation of the anomalous dispersion seems feasible, however, only on the assumption of a change in the association of the esters, not only in the homogeneous state on increase of temperature, but also on solution in various solvents.

A "characteristic diagram" for *d sec.*-octyl acetate was therefore constructed according to the method of Armstrong and Walker (*loc. cit.*). A reference line with slope of unity was drawn, and on it were plotted the various numbers representing the specific rotatory powers for mercury-green light. The numbers representing the specific rotatory powers for sodium-yellow and mercury-violet lights were then plotted on the ordinates passing through the points previously located on the reference line. The various points for the latter two lights were found to lie on two straight lines, and the diagram was similar in character to those for the substances of previously known anomalous dispersive power as drawn and described by Armstrong and Walker.

It is now found, however, that this same "characteristic diagram" can be used to co-ordinate the results of *all* the determinations of rotatory power of one of the two optically active forms of the hundred synthetical com-

pounds previously described by the present authors; thus the numerical results (varying from +50 to −25) of the determinations of rotatory power for the three lights in different solvents at all concentrations and in the homogeneous state at different temperatures, not only of one compound, but of many (all of which are of very simple, but closely related constitution), have been plotted on one diagram. In this the various values lie on three straight lines, which intersect above the zero-line, and not all at one point. The dispersions then appear in the diagram as some function varying with the magnitude of the rotatory powers, thus co-ordinating the small, but very definite, differences in the dispersions of the homologous compounds which have been observed experimentally.

It cannot yet be said whether this co-ordination is due either (i.) to the comparison of a large number of compounds which have very similar dispersive powers, or (ii.) to the closely related constitutions of the substances.

This method of plotting appears to afford (in some cases at least) a means by which a derivative differing in sign from that of the optically active parent substance can be properly designated "*d*" or "*l*," and also a means of determining whether a change in configuration has taken place in the formation of a derivative.

Discussion.

Sir W. Ramsay suggested that the cause of rotation was ultimately in the direction of the circular motion of electrons within the molecule. A dextrorotatory substance, say, might have hydroxy in the molecule, capable of repelling an electron, and causing it to rotate dextrorotatorily. On the other hand, if the hydroxyl be replaced by bromine, the bromine atom might have the property of attracting an electron and of reversing the direction of its rotation. This suggestion was made, not with any conviction of its applicability, but merely for consideration as to whether it was possible to obtain any clue to the fundamental reason of rotation.

*288. "*The Interaction of Sodium Amalgam and Water.*" By Herbert Brereton Baker and Leslie Henry Parker.

Water distilled under special conditions has a visibly slower rate of action on sodium amalgam than ordinary distilled water. An apparatus was constructed to measure accurately the hydrogen evolved, and various samples of water were tested. The least active specimens of water were obtained by distillation from copper or platinum apparatus, especially on superheating the steam before the latter was condensed.

The rate of action was shown to be no function of the conductivity of the water used, but was found to depend largely on the pressure at which the reaction was conducted, increase of pressure causing the rate of action to diminish, and *vice versâ*. Various explanations of this phenomenon were put forward and tested, but the only feasible one was the assumption of the presence of some impurity in minute quantity, which was volatile under the conditions of ordinary distillation, but was destroyed on heating to redness. Experimental evidence was adduced which seemed to show that the only impurity which satisfied all the conditions was hydrogen peroxide, and the widely differing activities of various samples of water on sodium amalgam is ascribed to the presence of varying quantities of hydrogen peroxide.

*289. "*The Action of variously treated Waters on Sodium Amalgam.*" By Leslie Henry Parker.

Further evidence was adduced in support of the explanation of the varying activity of different samples of water on sodium amalgam put forward by Baker and Parker (preceding paper).

Various metals were sealed up with a quantity of the inactive water for definite periods. Metals such as copper, mercury, &c., did not have much effect, whilst aluminium increased the activity of the water on sodium amalgam. This was shown to be in harmony with Traube's work on the wet oxidation of metals (*Ber.*, 1882, xv., 670). Exposure to radium bromide also increased the activity. This is in accordance with the work of Kailan (*Monatsh.*, 1912, xxxiii., 1329).

Discussion.

Dr. Senter suggested that the results would probably come under the heading of over-voltage phenomena, the best-known example of which was the retarded action between pure zinc and sulphuric acid. Over-voltage at the boundary between solid and liquid appeared to be connected with surface tension, and it might be assumed that the active substance, whatever it might be, modified the surface tension.

With reference to the author's proof of the presence of hydrogen peroxide in tap water, tests depending on the liberation of iodine from iodides were rather untrustworthy, as in certain circumstances dissolved oxygen gave the reaction in question. The titanium dioxide test was trustworthy, and was extremely sensitive, as it was capable of detecting 1 part of peroxide in 50 million parts of water (compare Senter, *Trans. Faraday Soc.*, 1906, ii., 142), and the fact that it was not given by the water in question appeared to render further investigation desirable. The effect of added hydrogen peroxide might be connected with the fact that this compound was readily decomposed at a mercury surface (Bredig); the evolution of oxygen would presumably disturb the very unstable equilibrium characteristic of over-voltage.

Dr. R. E. Slade agreed that it was to be expected that hydrogen peroxide would disturb the over-voltage at the surface of the amalgam in the manner suggested by Dr. Senter. He believed, however, that a very important factor was the existence of dust particles in the water, and quoted the work of G. N. Lewis on the potential of sodium amalgams in support of this. The experiment which Mr. Parker has just shown rather pointed to this theory, for in the tube of pure water the bubbles of hydrogen came off at a few points which moved about on the surface of the amalgam. Perhaps the superheating of the steam was an efficient way of removing particles of dust by destroying them or by causing them to adhere to the hot tube.

Dr. Keane asked whether the influence of light had been studied in connexion with the experiments described, as this might have considerable effect both in regard to the production and decomposition of hydrogen peroxide.

In reply to Dr. Senter, Mr. Parker said that no comparative experiments had been made as to the relative values of the tests for hydrogen peroxide: further experiments were in progress with the view of obtaining some light on the mechanism of the reaction. In reply to Dr. Keane, he also stated that no experiments had been tried on the influence of light on the reaction.

*290. "*The Polymerisation of Cyanamide.*" By George Francis Morrell and Peter Burgen.

The polymerisation of cyanamide, under various conditions, both in the solid state and in solution, and also under the influence of catalysts, has been quantitatively studied. With the pure substance itself only about 10 per cent was found to have changed in six months, and in aqueous solution, even at elevated temperatures, the reaction proceeds comparatively slowly, many hours' heating at 100° being required to complete it. In absolute alcoholic solution the reaction-velocity is much further reduced. In all these cases the velocity-constant was not that of a bimolecular reaction, but equal amounts were found to be changed in equal intervals, except at great dilution, in which case a logarithmic curve was obtained. An ionic explanation may be advanced to explain these facts, the ions present in very small and, at first, practically constant concentration alone taking part in the change. The influence of acids and bases, such as sulphuric acid, ammonia, and sodium hydroxide, as catalysts produces an extremely marked acceleration, very small quantities reducing the period of half-change in aqueous solution at 100° from about twelve hours to as many

minutes. Increasing quantities of sodium hydroxide produced increasing acceleration up to a point corresponding with the addition of 0·25 equivalent, but the further addition brought about a slight retardation, so that a solution containing sodium cyanamide, although it polymerised much more rapidly than pure cyanamide (half period at 100°, thirty minutes, compared with twelve hours in the latter case), yet did not do so more quickly than one containing less than 1/30th of the amount of hydroxide. The velocity-constant of these reactions was found to be between that of a unimolecular and of a bimolecular reaction, which latter stage it would only reach, on the authors' hypothesis, at infinite dilution and complete ionisation.

DISCUSSION.

Dr. MORRELL, in reply to Dr. Forster, stated that the method found most satisfactory for isolating cyanamide from its sodium salt was to neutralise a well-cooled concentrated aqueous solution of the latter with oxalic acid. The precipitated sodium oxalate was filtered off, and the filtrate evaporated almost to dryness in a vacuum. From this residue the cyanamide was extracted with ether, in which other substances present were insoluble. It was finally purified by recrystallisation from the same solvent.

*291. "*Some Derivatives of Oleanol.*" By FRANK TUTIN and WILLIAM JOHNSON SMITH NAUNTON.

Oleanol, $C_{31}H_{50}O_3$, a crystalline substance from olive leaves (Power and Tutin, *Trans.*, 1908, xciii., 896), has been further investigated. On oxidation with potassium permanganate it yields *oleanone*, $C_{29}H_{44}O_2(OH)_2$, which gives a *mono-* and *di-acetyl* derivative.

Oleanone, when heated with dilute acetic acid, undergoes a profound change, the reaction products containing a *substance*, $C_{50}H_{76}O_7(OH)_2$. An analogous change occurs when diacetyloleanone is heated with a mixture of acetic and hydrochloric acids. The *monoacetyl* derivative, $C_{50}H_{76}O_8(OH){\cdot}CO{\cdot}CH_3$, thus produced, on hydrolysis with alkali, yields the above-mentioned dihydroxy-compound.

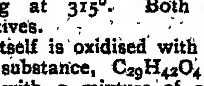
On oxidation with chromic acid, oleanone yields a *substance*, $C_{29}H_{41}O_3{\cdot}OH$ (m. p. 275°), which, when heated for two hours with alcoholic alkali, gives an *isomeride*, melting at 315°. Both substances yield *monoacetyl* derivatives.

When oleanol itself is oxidised with chromic acid the above-mentioned substance, $C_{29}H_{42}O_4$ (m. p. 275°), is formed, together with a mixture of at least three *carboxylic acids*.

292. "*Some Derivatives of Phorone.*" Part I. By FRANCIS FRANCIS and FRANCIS GEORGE WILLSON.

An investigation of some derivatives of phorone has been commenced by the study of a phorone dibromide obtained from the tetrabromide by the action of pyridine.

The most characteristic reaction of this dibromide is the ease with which it is converted by concentrated sulphuric acid into a crystalline derivative, a study of the oxidation and reduction products of which has led to the conclusion that it is *4-bromo-2 : 2 : 3 : 3-tetramethyl*bicyclo [0, 1, 2]*pentan-1-ol-5-one*,



The oxidation and reduction products were described; among the former is tetramethylsuccinic acid, and among the latter, 1 : 1 ; 2 : 2-*tetramethyl*cyclo*pentan-4-one*, a substance with properties curiously similar to those of camphor.

The derivative also gives rise on bromination to a *dibromide* possessing characteristic properties.

293. "*The Porosity of Iron.*" By WILLIAM HUGHES PERKINS.

An attempt has been made to correct or confirm the conclusion of Friend that iron is slightly porous (*Trans.*, 1912, ci., 50). It is concluded that only very small quantities of the alkalis, and therefore presumably of other salts, are retained under prolonged washing. The quantity of ammonia retained by iron after about fifteen to twenty minutes' washing is probably not more than about 0·0000001 grm. per sq. cm.

294. "*The Bleaching Action of Hypochlorite Solutions.*" By SYDNEY HERBERT HIGGINS.

Bleaching powder solution to which an excess of boric acid has been added has very energetic bleaching properties because the boric acid merely liberates hypochlorous acid from the hypochlorite, whereas an excess of hydrochloric acid produces free chlorine and a solution of very weak bleaching properties. If, however, calcium carbonate is added to the latter solution, hypochlorous acid is regenerated, and the bleaching properties are restored. The addition of hydroxides to hypochlorite solutions opposes the hydrolysis of the hypochlorite, and retards the bleaching action, whereas the addition of small quantities of acids assists the hydrolysis and stimulates the bleaching action; the effect on the bleaching properties of the solution is due to the active mass of the free hypochlorous acid present, being in the one case reduced and in the other augmented. Even in the presence of a large excess of hydroxides the solutions have a small bleaching effect, which is probably due to a small amount of hypochlorous acid being still present in solution in spite of the opposition of the hydroxide to the hydrolysis of the metallic hypochlorite. All the experiments point to the conclusion that hypochlorite solutions entirely owe their bleaching properties to the free hypochlorous acid present in solution. Sometimes there is a secondary reaction between the hypochlorous acid and any neutral chloride present, producing nascent chlorine of energetic bleaching properties ((*Proc.*, 1912, xxviii., 130), but the main action is one of direct oxidation by the hypochlorous acid. During the bleaching action chlorides are produced by the reduction of the hypochlorites, but the stimulating effect of chlorides thus produced on the bleaching action is negligible.

295. "*Guaiacum Resin as a Reagent for the Detection of Oxydases and of Minute Traces of Copper.*" By WILLIAM RINGROSE GELSTON ATKINS.

In order to ascertain how far traces of metals might vitiate tests for oxydases by guaiacum resin, a series of experiments was carried out to determine the limits of sensitiveness of the reaction towards certain salts. Adopting the methods usual in water analysis, it was found that very minute amounts of copper salts or of potassium permanganate may be detected by this test. Accordingly it is brought forward as a reaction of utility in water analysis. Below are recorded the limits of sensitiveness of the reaction, expressed in grms. per cc. Copper as sulphate, 2×10^{-9} to 2×10^{-8}. Potassium permanganate, 4×10^{-8}. Potassium dichromate, 1×10^{-7}. Iron, as ferrous sulphate, 1×10^{-6}, as ferric sulphate, 1×10^{-6}. Lead as acetate, 6×10^{-6}. Nitric acid, $2\times{}^{-5}$. Manganese as sulphate, 8×10^{-4}. In each case a few drops of hydrogen peroxide were added, as well as a very dilute solution of the reagent. Traces of chlorides were also present, and play an important part.

296. "*The Absorption Spectra of various Derivatives of Pyridene, Piperidine, and Piperazine in Solution and as Vapours.*" By JOHN EDWARD PURVIS.

The absorption spectra of a number of the derivatives of pyridine, piperidine, and piperazine, both in solution and in the vaporous condition, have been investigated. The general results show that, besides the nature of the molecule, the type, the number, and the orientation of the side-chains influence the production of the narrow vapour bands; and that, when these bands disappear, the remaining bands are generally comparable with the solution bands.

297. "*Derivatives of* p-*Iodoaniline.*" By FREDERICK DANIEL CHATTAWAY and ALFRED BERTIE CONSTABLE.

The ease with which chlorine and bromine substitute arylamines has led to a very complete knowledge of the simpler derivatives which they form, but comparatively few of the corresponding iodine compounds have been prepared on account of the difficulty of effecting iodine substitution and the readiness with which the iodoanilines decompose.

The conditions necessary to obtain a good yield of *p*-iodoacetanilide, and from it to prepare *p*-iodoaniline, were described. The aniline having been obtained in quantity, a number of its simpler derivatives have been prepared.

298. "*The Interaction of Tetranitromethane and Compounds containing Centres of Residual Affinity.*" (Preliminary Note). By ERNEST MAGOWAN HARPER and ALEXANDER KILLEN MACBETH.

The work was undertaken to investigate the colours developed on adding tetranitromethane to various substances. Ostromisslensky (*Journ. Prakt. Chem.*, 1911, [2], lxxxiv., 349) has recorded such effects with aromatic amines, and also with aliphatic compounds containing the ethylenic double linking. Clarke, Macbeth, and Stewart (*Proc. Chem. Soc.*, xxix., 161) have shown that these are only particular cases of a more general phenomenon. Colours have been obtained with organic sulphides, iodides, phosphines, amino-compounds, &c.

The method employed was to photograph tetranitromethane in an alcoholic solution of the substance of constant strength. Tetranitromethane itself gives no colour in dry alcohol. With the sulphides a yellow colour is produced on mixing the solutions, but the absorption spectrum does not differ greatly from that of tetranitromethane. The colour deepens on keeping, and after some time the spectrum undergoes a great change. A band is developed in the region $1/\lambda$ 2800—2900; thus tetranitromethane with N/10-pentamethylene sulphide after fourteen hours shows a band the head of which is at $1/\lambda$ 2850 in the log-thickness 35 of N/100,000 solution.

With compounds containing an ethylenic double bond a similar band is obtained; thus tetranitromethane with N/10-amylene after five days gives a band the head of which is at $1/\lambda$ 2850 in the log-thickness 32 N/100,000-solution.

Similar bands are obtained with sulphur compounds other than the sulphides (ethyl mercaptan, &c.), and with various aliphatic amino-compounds, the band development being exceptionally rapid in these cases.

In most cases the penetration of the band increases with time, thus:—

	Band head.	Log-thickness N/100,000.	Time. Days.
N/10-amylene	$1/\lambda$2850	32	5
N/10-amylene	$1/\lambda$2850	26	10
N/10-pentamethylene sulphide	$1/\lambda$2850	33	2
N/10-pentamethylene sulphide	$1/\lambda$2850	28	5

It appears that the solvent plays a very important part in the action. In light petroleum no band was obtained with tetranitromethane and amylene. The spectrum after five days and after fourteen days was the same.

Further, it would appear that there is in this way a means, not only of detecting, but also of comparing, the residual affinities of different substances; thus the different sulphides give bands of different penetrations in equal times, for example:—

		Log-thickness N/100,000.	Days.
N/10-pentamethylene sulphide	Head of band	28	5
N/10 propyl sulphide	"	30	5
N/10-thioxan	"	31	5

A similar effect holds in the case of other classes of compounds.

With regard to the nature of the reaction, nitromethane was substituted for tetranitromethane with negative results. Investigations are being continued with other mononitro-compounds, in which the hydrogen atoms are replaced by chlorine and other electro-negative atoms. Dinitro- and trinitro-compounds are also being substituted. The effect of introducing electro-negative atoms into the molecule containing the centre of residual affinity is also being studied.

299. "*The Relative Activities of certain Organic Iodo-compounds with Sodium Phenoxide in Alcoholic Solution.* Part III. *The Temperature Coefficients.*" By DAVID SEGALLER.

The velocity-coefficients of the following alkyl iodides, methyl, ethyl, propyl, *iso*propyl, butyl, *iso*butyl, *sec.*-butyl, *tert.* butyl, amyl, *iso*amyl, *sec.*-amyl, hexyl, *sec.*-hexyl, heptyl, *sec.*-heptyl, octyl, *sec.*-octyl, and cetyl iodides have been measured with sodium phenoxide in alcoholic solution at four different temperatures, and the temperature coefficients determined.

It is found that the results obtained are in good agreement with the equation of Arrhenius (*Zeit. Phys. Chem.*, 1889, iv., 226). The results show that the relative activities of the alkyl iodides are approximately independent of the temperature.

300. "*Resolution of* α-*Anilinostearic Acid.*" By HENRY RONDEL LE SUEUR.

α-Anilinostearic acid has been resolved into its optically active components by crystallisation of its *l*-menthylamine salt.

d-α-*Anilinostearic acid* melts at 129—130°, and has $[\alpha]_D$ 19 +34·7° in solution in pyridine, and $[\alpha]_D$ 40 +18·6° in solution in alcohol. The lævo-acid has also been isolated, and its properties are the same as those of its dextro-isomeride.

301. "*The Conversion of* d-*Glucosamine into* d-*Mannose.*" (Preliminary Note). By JAMES COLQUHOUN IRVINE and ALEXANDER HYND.

In previous communications (*Proc.*, 1912, xxviii., 54; *Trans.*, 1912, ci., 1128), the authors have already described the conversion of *d* glucosamine into *d*-glucose. They have now succeeded, by a process which on first inspection seems more direct, in transforming the amino-sugar into *d*-mannose.

Methylglucosamine hydrochloride, when gently warmed with excess of benzaldehyde, passes gradually into solution when the liquid is saturated with dry hydrogen chloride. The product of this reaction is *benzylidenemethylglucosamine hydrochloride* (m. p. 205° with decomposition; $[\alpha]_D$ 20 −54·4° in methyl alcohol), which is formed by condensation of the aldehyde with two hydroxyl groups of the sugar, and is thus comparable with the benzylidene-methylglucoside described by Alberda van Ekenstein. The compound is exceedingly unstable towards acids, and, when acted on by silver nitrite, loses not only the amino-group, but also the benzylidene residue and the glucosidic group. Chitose is thus the ultimate product of the reaction.

In order to avoid this disruption of the molecule, the amino-group was removed by the addition of excess of sodium nitrite in dilute aqueous solution. In this way the reaction of the system was kept continuously alkaline, and, although the glucosidic group was eliminated, the hydrolysis of the benzylidene residue was avoided, and thus chitose formation was excluded. During the reaction nitrogen was vigorously evolved, and a sparingly soluble product was rapidly precipitated. This proved to be a derivative of a reducing sugar, and was characterised as *monobenzylidenemannose* (m. p. 144—145°; $[\alpha]_D$ 20 −22·4° in acetone). As the reducing group of the parent aldose is unsubstituted in this compound, the substance represents a new type of sugar derivative. On treatment with very dilute hydrochloric acid, the compound was easily hydrolysed, with the formation of *d*-mannose, which was identified by determination of the specific rotation and by con-

version into crystalline derivatives, such as methylmannoside and mannoseanilide.

The individual steps of the process outlined above appear to proceed practically quantitatively, and are summarised below:—

d-Glucosamine → methylglucosamine hydrochloride → benzylidenemethylglucosamine hydrochloride → benzylidenemannose → *d*-mannose.

It was shown that the formation of *d*-mannose as the final product cannot be attributed to the well-known action of alkali in effecting the conversion of closely related reducing sugars. Glucosamine may thus be converted into either *d*-glucose or *d*-mannose, and in one of the two processes a change of the nature of a Walden inversion must take place. The evidence at present available indicates that the change in configuration probably occurs during the decomposition of benzylidenemethylglucosamine by nitrous acid, and there seems no necessity to modify the claim made in a previous paper (*loc. cit.*) that glucosamine is a derivative of *d*-glucose.

302. "*The Mechanism of Denitrification.*" By WILLIAM HULME.

A series of experiments, conducted with a view to investigate the mechanism of denitrification, showed that this reduction might be divided into two parts, namely, (1) the bacterial reduction, and (2) the enzymatic reduction.

The fermentation of similar media, one with and the other without potassium nitrate, under anaerobic conditions, showed the gas evolution to consist of nitrogen (98 per cent) and carbon dioxide from the nitrate-containing medium, and of hydrogen (70 per cent) and carbon dioxide from the nitrate-free medium. A medium containing only a very small percentage of nitrate evolved nitrogen and carbon dioxide as long as nitrate and nitrite obtained in the solution, but hydrogen and carbon dioxide appeared as soon as these had disappeared; thus the chemical agent by which the organism reduces the nitrate is nascent hydrogen.

The media were tested for enzyme action by precipitation with alcohol, drying, dissolving in water, and Chamberland-filtration, measured quantities of this solution being added to small quantities of a sterilised 1 per cent solution of potassium nitrate, and the nitrite produced being measured. The results showed a considerable reduction with the "product" obtained from the nitrate-containing flasks, whilst that obtained from the nitrate-free flasks was devoid of this reducing power.

These results were confirmed by a second series of experiments, in which the fermentation took place aerobically. The enzyme solutions in all cases were not affected by boiling.

The mechanism of denitrification may be, therefore, represented as follows:—

1. $C \ldots + H_2O + \text{organism} = CO_2 + H_2 + \ldots$

or—

$CH_2 \ldots + O_2 + \text{organism} = CO_2 + H_2 + \ldots$

where C represents the carbon of the nutrient substance.

2. $KNO_3 + \underset{(\text{Enzyme})}{E} = KNO_2 + EO$.

$EO + 2H = E + H_2O$

$2KNO_2 + 5H + 2CO_2 = 2KHCO_3 + 4H_2O + N_2$,

thus accounting for the large percentage of nitrogen in the gases evolved from the nitrogen-containing flasks.

303. "*The Catalytic Activity of Acids. Evaluation of the Activities of the Hydrogen Ion and the Undissociated Acid.*" By HARRY MEDFORTH DAWSON and FRANK POWIS.

The catalytic activity of a series of acids has been examined by measurements of the velocity with which acetone passes from the ketonic to the enolic form in aqueous solutions of determinate acid concentration. The results obtained are entirely at variance with the theory that the catalysing activity of an acid is determined by its hydrogen-ion concentration, for the ratio of the reaction-velocity to the ionic concentration varies to a large extent when the concentration of the acid is changed. The observations are, however, in good agreement with the view that both the non-ionised and ionised forms of the acid take part in the acceleration of the reaction, the actual catalytic effect being additively composed of the effects due to the two components.

The activity of the non-ionised acid diminishes rapidly as its tendency to ionise decreases; this is clearly shown by the following numbers, which express the activities in terms of that of the hydrogen ion:—Hydrochloric, 1·77; dichloroacetic, 0·50; αβ-dibromopropionic, 0·152; chloroacetic, 0·056; acetic, 0·0034. As yet it does not seem possible to say whether these ratios are independent of the nature of the catalysed reaction.

304. "*The Configuration of the Doubly linked Nitrogen Atom. Optically Active Salts of the Semicarbazone and Benzoylphenylhydrazone of* cyclo-*Hexanone-4-Carboxylic Acid.*" By WILLIAM HOBSON MILLS and ALICE MARY BAIN.

The method which the authors used in order to investigate the configuration of tervalent nitrogen in the oximino-group (*Trans.*, 1910, xcvii., 1866) has been further employed for the examination of the configuration of the doubly-linked nitrogen in the hydrazone group, $:N\cdot NR_1R_2$. cyclo *Hexanone-4-carboxylic acid benzoylphenylhydrazone* has been obtained in an optically active form by crystallisation of its *quinine* salt from dilute methyl alcohol. The sodium salt obtained by treating the quinine salt with sodium hydroxide was strongly dextrorotatory, having $[M]_D 238\cdot6°$.

Dextrorotatory salts of *cyclo*hexanone-4-carboxylic acid semicarbazone (W. H. Perkin, *Trans.*, 1904, lxxxv., 427) were obtained similarly with the aid of morphine, the molecular rotations observed varying from $[M]_D 37\cdot8°$ to $27\cdot9°$ in different preparations.

The active salts of both compounds showed marked autoracemisation on keeping, the loss of activity being much more rapid in the case of the semicarbazone than in that of the benzoylphenylhydrazone. The autoracemisation was checked by the addition of alkali hydroxides, sodium and potassium hydroxides being much more effective than ammonia. On acidification the activity in both cases instantly disappeared. These results can only be satisfactorily explained by regarding the molecular asymmetry of these compounds as being of the centro-asymmetric type, and due to the fact that when the carbonyl oxygen of the symmetrical keto-acid is replaced by the hydrazone residue, $:N\cdot NR_1R_2$, the $\cdot NR_1R_2$ group takes up a position outside the original plane of symmetry of the keto-acid. Accordingly, in these hydrazones, the three valencies of the doubly-linked nitrogen atoms do not lie in one plane, but are directed along the three edges of a trihedral angle.

NOTICES OF BOOKS.

Metallography. By CECIL H. DESCH, D.Sc.(Lond.), Ph.D.(Würzb.). Second Edition. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1913.

THE latest results of recent investigations are incorporated in the second edition of this valuable book. The chapter on the physical properties of alloys has been much enlarged and modern work on the metallography of iron and steel is considered in some detail. The appendix, which has been carefully brought down to date, is a very useful feature. It contains details of all the binary and ternary systems of which equilibrium diagrams have been published, and in every case a reference is given to the most recent complete study of the system, or if there is any doubt about the accuracy of the work to an earlier but more trustworthy investigation.

The Absorption Spectra of Solutions as Affected by Temperature and by Dilution: A Quantitative Study of Absorption Spectra by Means of the Radiomicrometer. By Harry C. Jones and J. Sam Guy. Washington, D.C: The Carnegie Institution. 1913.

The ultimate aim of the researches described in this monograph was to discover whether the free electrons of the ion have anything to do with its power of absorbing light, and for this purpose, since the absorption spectra in the region of the wave-lengths which are much greater than 0·8 μ had to be studied, the grating spectrograph was useless. The radiomicrometer, however, as modified by Dr. Guy, was sufficiently sensitive to be employed for the determinations, and with its aid the absorption spectra of a number of salts were mapped. The book contains plates showing the results obtained with about fifty solutions of neodymium, uranium, and praseodymium salts, with detailed descriptions of the use of the instrument. A remarkable fact has been brought to light by the research, namely, that aqueous solutions of hydrated salts are often more transparent than pure water, and apparently combined water has less power to absorb light than free or uncombined water.

Standard Metric Equivalent Tables. Published by the Central Translations Institute, Davies Inn House, 265, Strand, W.C.

The above collection of metric equivalent tables have been neatly printed on card, and will be found useful in the office or works where money, weights, or measures need to be changed from one system into the other. Seventy different tables are given; one side of the card is occupied with weights and measures, the other side with coinage; the tables in this form can be fixed to the side of the desk or the wall, and are much more easy for reference than when in a book.

CORRESPONDENCE.

PASSIVITY OF METALS.

To the Editor of the Chemical News.

Sir,—In the issue of your paper for November 21, 1913, there is a very interesting article by George Senter on the passivity of metals. It gives a good *resumé* of what has been done on the subject. It seems to me, however, that the valency theory has been a little overlooked. On page 251 the matter is dismissed with a few words:—"The valency theory has met with very little support during the last four or five years, and therefore need not be further considered here."

In this connection I wish to point out a rather remarkable numerical coincidence, which to my mind proves beyond dispute that the true formula for the common form of iron, as we know it, at ordinary temperatures, the a ferrite, is $Fe_2^{III}—Fe_3^{II}$, or a compound of ferrous and ferric atoms.

If we assume this formula, then α-ferrite would contain 60 per cent of *ferrous* iron. Now, the magnetic iron oxide has the formula Fe_3O_4 or FeO,Fe_2O_3, containing 24·138 per cent of *ferrous* iron. The ratio between the ferrous iron in α-ferrite, and in the magnetic oxide of iron, is therefore as 60 is to 24·138, or as 1 is to 0·40230.

When Plücker compared the magnetic permeability of iron with that of its magnetic oxide, he found that the ratio was as 1 is to 0·40227.

For reasons I cannot go into at present, and which I expect to publish later, I am convinced that the magnetism of metallic iron and of its magnetic oxide must be due to the ferrous atoms alone. This led me to notice the coincidence above mentioned a little over a year ago.—I am, &c.,

Hjalmar Westling.

309, Union Square Buildings,
San Francisco, Cal., Dec. 6, 1913.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Bulletin de la Société Chimique de France,
Vol. xiii.-xiv., No. 18—19, 1913.

Influence of Constitution on the Thermic Properties of Binary Mixtures.—Paul Pascal and Léon Normand.—Mixtures of two substances of symmetrical structure always give mixed crystals in all proportions when the nuclear structure is the same in both compounds. Two symmetrical substances always exhibit isodimorphism when the nature of the nuclei in them is not the same. Dissymmetry of structure in the central part of the molecule (not nuclear) causes the disappearance of isomorphism, and isodimorphism appears, whatever the nuclear part of the molecule may be. Dissymmetry of nuclear structure produces the same effects as dissymmetry of the fatty central chain.

Condensation of Phenylisoxalone with Mesoxalic Ether.—André Meyer.—One molecule of mesoxalic ether condenses with 2 molecules of phenylisoxazolone, 1 molecule of water being eliminated:—

$$2C_9H_7O_2N + CO(CO_2C_2H_5)_2 = H_2O + C_{23}H_{22}O_8N_2.$$

The product is the mesoxalate of ethyl bis-phenylisoxazolone, which readily yields diethyl, diacetyl, and dibenzoyl derivatives. The ether behaves like the hydrate of the ketone $(OH)_2 = C = C = (CO_2C_2H_5)_2$.

Action of Acids on Alcoholic Fermentation.—M. and Mdme. Rosenblatt.—The authors have found that the following substances have no favourable action on alcoholic fermentation:—Hydrochloric, formic, acetic, propionic, *n*-butyric, sulphuric, tartaric, citric, and phosphoric acids, and monopotassium sulphate. Experiments with monopotassium phosphate, oxalate, and citrate, dipotassium citrate, and monosodium tartrate, however, show that they influence alcoholic fermentation favourably.

Determination of Methyl Alcohol and Formic Aldehyde present in Small Quantities in the same Solution.—Maurice Nicloux.—A given volume of the mixture is oxidised by bichromate and the quantity of bichromate used is determined. In a second experiment the quantity of CO_2 produced is estimated. The reactions—

$$CH_3OH + K_2Cr_2O_7 + 4H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + CO_2 + 6H_2O,$$

$$3HCOH + 2K_2Cr_2O_7 + 8H_2SO_4 = 2SO_4K_2 + 2Cr_2(SO_4)_3 + 3CO_2 + 11H_2O,$$

show that 32 mgrms. of methyl alcohol require 294 mgrms. of $K_2Cr_2O_7$ and give 44 mgrms. of CO_2. Also 30 mgrms. of aldehyde require 196 mgrms. of $K_2Cr_2O_7$ and give 44 mgrms. of CO_2. If x = quantity of alcohol, y = quantity of aldehyde, a = quantity of CO_2 produced by 5 cc. of the mixture which rrequired b of bichromate $\frac{44x}{32} + \frac{44y}{30} = a$ and $\frac{294x}{32} + \frac{196y}{30} = b$.

Methyl Alcohol in Leaves.—Maurice Nicloux.—By the method described in the foregoing article the author has determined the amounts of methyl alcohol and of aldehyde in the products obtained by distilling leaves. His experiments showed that methyl alcohol was always present, while the presence of aldehyde was problematical. He suggests that the formation of methyl alcohol may be due to the equation $CO_2 + 2H_2O = CH_3OH + O_3$.

MEETINGS FOR THE WEEK.

Wednesday, 14th.—Royal Society of Arts, 5. (Juvenile Lecture): "Electric Vibrations and Wireless Telegraphy," by R. P. Howgrave-Graham, M.I.E.E.

Thursday, 15th.—Royal Society of Arts, 4.30. "Indian Museums—a Centenary Retrospect," by Col. T. Holbein Hendley, C.I.E.

Erratum.—Vol. cviii., p. 318, col. 1, line 20, *for* "Distillation of Oil" *read* "Distillation of Coal." And, in same paragraph, "fatty oil" should read "fat coal."

THE CHEMICAL NEWS.

VOL. CIX., No. 2825.

THE PHOTO-ELECTRIC BEHAVIOUR OF IRON AND THE THEORY OF PASSIVITY.*

By H. STANLEY ALLEN, M.A., D.Sc.,
Senior Lecturer in Physics at University of London, King's College.

IT is not unusual to find that investigations in one branch of science serve to throw light on problems connected with some other subject. The present research was undertaken in the hope that the study of the physical phenomenon of photo-electricity might assist in elucidating the century-old problem of the nature of "passivity." The photo-electric effect here referred to is that which is known as the Hertz-Hallwachs effect (see Note). It consists in the loss of a negative electric charge or the acquisition of a positive electric charge by an insulated metal plate when the surface of the metal is illuminated. The experiments of J. J. Thomson and of Lenard have proved that the essential point in this electric change is the emission of negative electrons from the metal surface when the latter is exposed to light. In a high vacuum the current is carried by the electrons, in a gas the current is carried by ions formed by the association of the electron with one or more gaseous molecules. It is necessary to emphasise the fact that this separation of electrons is not the result of a chemical change, such as oxidation. The experiments of Elster and Geitel and many other investigators have shown that the photo-electric discharge takes place from the surface of the alkali metals in the highest attainable vacuum or in an atmosphere of argon or helium, and that such "photo-electric cells" retain their activity unchanged over periods of months or years. In this case the presence of a trace of oxygen would result in the formation of a layer of oxide which would effectively mask the phenomenon. The photo-electric current is due to the direct action of the electro-magnetic waves of light on the electrons of the metal; the energy of the light goes to increase the kinetic energy of the electron until the kinetic energy becomes sufficiently great to overcome the forces of attraction, tending to prevent the escape of the electron.

(NOTE.—We are not concerned in this paper with the photo-electric cells studied by Becquerel and Minchin, in which the potential difference between metal electrodes immersed in an electrolyte is altered by exposing one of the plates to light. Such changes may be regarded as secondary effects, while the change that we are considering is the primary photo-electric action.)

In a paper read before the Royal Society of London I have given an account of experiments on the photo-electric behaviour of iron in the active and passive state. A polished iron plate exposed to ultra-violet light rapidly loses a negative electric charge. By finding the saturation current produced when an electric field of sufficient intensity is applied, we obtain a measure of the photo-electric activity of the metal.

Dry passive iron can be obtained by using the method described by Heathcote (*Journ. Soc. Chem. Ind.*, 1907, xxvi., 899). Experiments were made with plates of Kahlbaum's sheet iron (0·2 mm. thick) and with rods of commercial iron and steel. It was found that iron which was chemically active was active in the photo-electric sense; iron rendered passive, either by the action of strong nitric acid or by use as anode in a voltameter containing dilute sulphuric acid, showed greatly reduced activity. The photo-electric activity after treatment was less than one half of the original value, and in some cases was too small to be detected. It should, however, be noted that iron which had been rendered passive generally showed a certain amount of photo-electric activity, so that, from the point of view of photo-electricity, passive iron shows varying, though small, degrees of activity. In these experiments the chemical activity was tested in solution, using dilute nitric acid (s.g. 1·2), whilst the photo-electric activity was measured with a dry surface. Attention must be drawn to the fact that the processes employed in changing the state of the iron were all wet processes. Muthmann and Frauenberger (*Zeit. Elektrochem.*, 1904, x., 929) state that "metals become passive on lying in the air, and their potentials (in KCl solution) assume medium values, whilst vigorous mechanical cleaning of the surface renders them active." Here the reference is to chemical activity, but the statement is equally true as regards photo-electric activity. Metals exposed to the air show "photo-electric fatigue," that is to say, their activity diminishes with an increase in the time that has elapsed since they were polished, whilst repolishing the surface gives rise to a large photo-electric current.

We appear to be justified in assuming a correlation between these two sets of phenomena, and in saying that the chemical activity and the photo-electric activity vary together. If this view be correct we see that there are *degrees* of activity and also of passivity, a conclusion which appears to be in accordance with the general experience of chemists. Further, we may regard the photo-electric fatigue sometimes observed with iron as a gradual passage from the active to the passive state.

We turn now to the bearing of these results on the interpretation of passivity. In view of the resemblance between the facts connected with photo-electric activity and fatigue and those relating to the passive state of metals, it is not surprising to find that the theories advanced as to the nature of the change accompanying photo-electric fatigue correspond closely with the explanations suggested for passivity (H. S. Allen, *British Assoc.* Reports, 1910; *Phil. Mag.*, 1910, xx., 572). In the table preceding the "Historical Note" these theories are given side by side.

The experiments of the author and others support the conclusion of Hallwachs that the dominant cause of fatigue is to be found in the condition of the layer of gas at the surface of the plate. So far, then, as this analogy serves, we should be inclined to attribute passivity to the surface film of gas.

We may, however, find more direct arguments in favour of the same view and against the other theories suggested.

The fact that from the photo-electric point of view different *degrees* of activity can be obtained from the same iron plate does not harmonise well with the idea of an allotropic change as the cause of chemical passivity; it agrees far better with the idea of a protective coating, whether of oxide or of gas, and best of all perhaps with the last named, *i.e.*, a gaseous film.

Byers (*Journ. Amer. Chem. Soc.*, 1908, xxx., 1718) in a useful summary of work done on passivity points out that "the contributors to the literature during the past ten years, with the exception of Haber and Goldschmidt, E. Müller and Spitzer, and Heathcote, unite in rejection of the Faraday view, if they fail to agree in any other particular." He regards the objections which can be urged against the existence of an oxide layer as "so convincing that we may well assent that the Faraday hypothesis may be laid to rest."

Putting on one side this view and also that which somewhat vaguely attributes passivity to the electric state of the surface, we are left to choose between the theory of an allotropic modification of the metal and the theory of the gaseous film.

Müller and Kœnigsberger (*Phys. Zeit.*, 1904, v., 413 797) found that the reflecting power of well polished iron

* A contribution to the General Discussion on "The Passivity of Metals," held before the Faraday Society, November 12, 1913.

remained unaltered when the iron was rendered passive. It was impossible to distinguish by optical means the presence of a layer of oxide, which must therefore, if present, be less than $\lambda/10$ in thickness. They support the view that passivity consists of the passage of a metallic modification of low valency into one of higher valency, but the experimental results do not seem inconsistent with the theory which attributes passivity to a gaseous film.

It has been objected to the gaseous-film theory of passivity that "a passive metal does not of necessity become active *in vacuo* (H. L. Heathcote, *Journ. Soc. Chem. Ind.*, 1907, xxvi., 899; J. N. Friend, "The Corrosion of Iron and Steel," p. 190). But it must be remembered that experience has repeatedly shown the impossibility of removing films of condensed gas from the surfaces of solid bodies merely by placing them in a high vacuum (compare F. S. Spiers, *Phil. Mag.*, 1900, xlix., 40; H. S. Allen, *Ibid.*, 1903, vi., 706; and also J. N. Friend, "The Corrosion of Iron and Steel," chap. v.).

If, then, we may regard the photo-electric behaviour of the metal as the criterion by which we may decide between the two principal theories, we are led to the conclusion that passivity is to be attributed to the condition of the gaseous film on the surface of the metal.

Theories of Photo-electric Fatigue.	*Theories of Passivity.*
1. A chemical change, such as oxidation of the surface.	Formation of a protective film of oxide. Formation of a layer of nitride.
2. A physical change of the metal itself.	An allotropic modification of iron. "Passive" iron trivalent; "active" iron, divalent.
3. Formation of an electrical double layer. (Lenard.)	"A permanent electric state of the surface." (Herschel.)
4. A disintegration of the metal due to the expulsion of electrons by light. (Ramsay and Spencer.)	
5. A change in the surface film of gas or in the gas occluded in the metal. (Hallwachs.)	An adherent surface film of gas which protects the iron from the action of the acid (see Note).

(NOTE.—An alternative form of this theory is to regard the normal state of pure iron as passive, and to attribute activity to hydrogen, probably in the ionic state.)

Historical Note.

In the more recent literature of "passivity" the oxidation theory is rightly attributed to Faraday, but the fact that the gaseous-film theory may equally claim the authority of his name has been overlooked. Faraday in his letter communicating the experiments of Schoenbein to the *Philosophical Magazine* (1836, [3], ix., 57) writes: "My strong impression is that the surface of the iron is oxidised, or that the superficial particles of the metal are in such relation to the oxygen of the electrolyte as to be equivalent to an oxidation."

In the August number (p. 122) he reviews some earlier observations on the *peculiar or altered* state of iron. Westlar "attributes the effect to the assumption of a negative electric state by the part immersed, the other part of the iron having assumed the *positive* state." Sir John Herschel "attributes the phænomena to a certain *permanent electric state of the surface of the metal.*" Professor Daniell suggests that the effect is due to a difference in the mechanical structure of the surface of the iron.

Thus even at this period we have representatives of the principal theories that have been advanced to account for passivity.

Schoenbein (*Phil. Mag.*, 1836, [3], ix., 259; 1837, x., 172) disagrees with Faraday's view. He says: "It is evident that the different action of the same nitric acid on iron is caused by a certain electrical state of the metal." Again, "That the iron (used as electrodes in nitric acid) is not partially oxidated is evident from its unchanged metallic lustre, as also from the proportions of gas given off at both wires, which I found according to several measurements to be as 1 to 2." In the second paper he directly attacks the oxidation theory, bringing forward many objections to it, and concludes: "All the reasons above given decide me to suppose that Faraday's views concerning the passive state of the iron do not explain it satisfactorily." In the same number Faraday replies emphasising the guarded character of his suggestion, which need not imply an actual oxidation but "a very delicate equilibrium of forces" where there is "association without combination." He agrees with Schoenbein that a satisfactory explanation of passivity has not been reached.

Thus it will be seen that Faraday's more guarded view is essentially the same as that which attributes the effects to the peculiar condition of the gaseous film at the surface of the metal.

To sum up our conclusions, we may say that iron which is chemically active shows large photo-electric activity, while processes which render iron passive greatly reduce this activity. These facts are in good agreement with the theory, which as well as the oxidation theory must be attributed to Faraday, that the cause of passivity is to be found in the condition of the gaseous layer at the surface of the metal.

THE CONSTITUTION AND STRUCTURE OF THE ELEMENTS.

By HAWKSWORTH COLLINS.

THE most regular row in the Periodic Table is the second containing the elements sodium, magnesium, aluminium, silicon, phosphorus, sulphur, and chlorine; and it must have been this row which was chiefly instrumental in producing the Periodic observation. A number of *facts* with regard to these 7 elements are now given in tabular form, followed by four observations upon them.

TABLE I.

Element.	At. wt.	Nearest whole number.	Number of parts the at. wt. is divided into.	Max. valency.
Na	23·00	23	1	1
Mg	24·32	24 = 23+1	2	2
Al	27·1	27 = 23+1+3	3	3
Si	28·3	28 = 23+1+3+1	4	4
P	31·04	31 = 23+1+3+1+3	5	5
S	32·07	32 = 23+1+3+1+3+1	6	6
Cl	35·46	35 = 23+1+3+1+3+1+3	7	7

1. Whenever the atomic weight of one of these elements is nearer to an even whole number its maximum valency is even; and whenever it is nearer to an odd whole number its maximum valency is odd.

2. A symmetrical arrangement of the whole numbers is possible, *with a portion 23 in each.*

3. The number of parts each whole number is divided into corresponds exactly with the valency of each.

N.B.—It is a chemical fact that one valency emanates from a mass of 23 (Na). It is also a fact that one valency emanates from a mass of 1 (H). Again, it is a fact that 2 valencies emanate from a mass of 4 (He). Therefore it is perfectly logical to say that, in the case of P, for instance, its 5 valencies emanate from the 5 portions 23, 1, 3, 1, and 3; with similar remarks for the other 6 elements.

4. When there is no portion (1+3, helium) present the

element is metallic, as in Na and Mg; but when this portion is present the element is non-metallic.

The above are four independent and exact observations to which there is no exception. The mathematical probability that any one of the four has happened by accident is $1:2^7$. Therefore the probability that the four observations together are the result of an accident is $1:2^{28}=1:268,435,456$.

The following six observations are also important:—

1. The atomic weights of all the 7 elements are either equal to or *greater than* the nearest whole numbers. This fact distinctly suggests that some impurity is liable to be present which causes some of the atomic weights to appear greater than they really are.

2. If helium could be given off from chlorine (35·46) with 7 valencies a portion would be left of atomic weight 31·46 with 5 valencies. Phosphorus (31·04) has 5 valencies.

If helium could be given off from phosphorus a portion would be left of atomic weight 27·04 with 3 valencies. Aluminium (27·1) has 3 valencies.

If helium could be given off from aluminium a portion would be left of atomic weight 23·1 with 1 valency. Sodium (23·00) has 1 valency. Again, if helium could be given off from sulphur (32·07) with 6 valencies, a portion would be left of atomic weight 28·07 with 4 valencies. Silicon (28·3) has 4 valencies.

And, if helium could be given off from silicon, a portion of atomic weight 24·3 would be left with 2 valencies. Magnesium (24·32) has 2 valencies.

3. Sir J. J. Thomson's X_3 could be given off from Cl, P, and Al.

4. Of all the metals sodium is *the* most likely to be a constituent part of other elements, since it is the most widely distributed metal.

5. The fact that the atomic weight of Cl is given as 35·46 instead of 35 does not upset the above argument at all, because we are considering the nearest whole numbers to the atomic weights.

6. It is quite possible that an atom of chlorine may have a special aptitude for condensing an abnormally large amount of protyle.

In the radio-active elements, whenever an atom of helium is given off with 2 valencies, the main portion loses 2 valencies; therefore it is evident that the helium atom was joined to the rest of the element by a non-chemically-evident force.

Besides, if it had been united with the remainder of the element merely by 1 or both of its valencies, the two parts would together have formed a chemical product, or molecule, and not an element. For instance, radium with 2 valencies splits up into helium with 2 valencies, and niton with no valency. Therefore helium was not united to niton by a valency, but by some other force; otherwise radium would be a chemical compound, niton-helium.

It follows from this that non-chemically-evident forces have been discovered by reasoning.

This deduction, together with all the above facts and observations, demonstrates that the constitution and structures of these seven elements is as follows, where the thin lines denote non-chemically-evident forces and the thick lines denote valencies. The structure of the portion 23 cannot be considered at present. (See Table II.).

The significance of this number 23 is now going to be extended. There are 83 elements recognised by the International Committee. The 10 of less atomic weight than 23 cannot come into the argument, and 14 others, La, Ce, Nd, Pr, Sa, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu, are rare elements, which cannot be considered in any way in relation to the others, because they cannot be placed in any satisfactory order in the Periodic Table. There are, therefore, 59 elements left for consideration. Thirty-four of the 59, *i.e.*, more than half, are concerned in Table III. and in the preceding matter.

The number 23 has an evident predominance in this table. The first 9 pairs are connected by the Periodic Observation. Hg is especially connected with Ag in mineralogy, and Cb with Ti. Cu is evidently connected with Ca, since they are both dyads, although the Periodic Table stands in the way. The chemical compounds of Rh are analogous to those of Fe, and the compounds of Ru are *exactly* analogous to those of Mn.

TABLE II.

Sodium	Na
Magnesium ..	Na—H
Aluminium ..	Na—H—H_3
Silicon	Na—H—H_3—H
Phosphorus ..	Na—H—H_3—H—H_3
Sulphur	Na—H—H_3—H—H_3—H
Chlorine	Na—H—H_3—H—H_3—H—H_3

Molybdenite (MoS_2) is especially found with cryolite (Na_3AlF_6) in Greenland. This fact would not be remarkable if one or both were common minerals, but they are both rare. The molecule MoF_6 is well known. Ga is *always* found with Al. The matrix of the element Ga is said to be "Si-Al-minerals from which most of the Na has been dissolved." (This statement undoubtedly suggests that Ga has been formed from the extracted Na). These facts show the connection between Mo, Ga, Al, and Na.

The last two elements, As and Cr, have no evident connection either in the Periodic Table or Mineralogy, but since their at. wts. are in accordance with the general rule about even and odd numbers, they are given here.

Now, owing to the discovery of the fact that protyle and X_3 can be given off from all sorts of substances, *it must be necessary to redetermine the ratio of the atomic weights of oxygen and hydrogen, after expelling all traces of these impurities.*

Another source of error exists in the fact that it is very difficult, or perhaps impossible, to entirely separate elements that are chemically alike. For instance, it is very difficult to obtain Cb free from Ti. The atomic weight of Cb is given as 93·5. Taking into consideration all the foregoing arguments, surely it cannot be very outrageous to say that all available evidence shows that the atomic weight of Cb is 94, and that of Ti 48, so that the difference is $46=2\times23$.

Again, suppose it is found that the 0·46 of the atomic weight of Cl (35·46) is due to protyle and X_3, then there will be large errors in those atomic weights, which are calculated from Cl.

In order to complete the argument with regard to pairs of like elements, it is necessary to give another table showing that the atomic weights of 8 pairs of elements have a difference of 90 (zirconium), which element can be shown to contain 3 atoms of sodium in its constitution. (Table IV.).

Zirconium (90·6) is especially connected in mineralogy with most of the above, and the elements of each pair are connected by the Periodic Observation.

It is much more likely that the differences are exactly the same than that they are nearly the same.

The three last tables concern 45 out of the 59 elements (*i.e.*, more than three-quarters) available for the argument.

It has now been shown that "the numbers 23 (Na) and 90 (Zr) connect the atomic weights of all or nearly all pairs of like elements." This is not intended to be the second main principle in the constitution and structure of the elements, which was referred to in the paper published in the CHEMICAL NEWS, November 14; but it must temporarily take the place of that principle, for it has been found impossible to get all the evidence required into a short paper.

TABLE III.

Element.	At. wt.	An element with which the former is especially associated in chemistry or mineralogy or both.	At. wt.	Difference in at. wt. of the associated elements.				Deductions.
Cadmium	112·40	Zinc	65·37	47·03	=	2 × 23·515	Cd	= Na_2Zn
Cæsium	132·81	Potassium ..	39·10	93·71	=	4 × 23·427	Cs	= Na_4K
Rubidium	85·45	Potassium ..	39·10	46·35	=	2 × 23·175	Rb	= Na_2K
Indium	114·8	Gallium ..	69·9	44·9	=	2 × 22·45	In	= Na_2Ga
Selenium	79·2	Sulphur . ..	32·07	47·13	=	2 × 23·565	Se	= Na_2S
Iodine	126·92	Chlorine. ...	35·46	91·46	=	4 × 22·865	I	= Na_4Cl
Antimony	120·2	Vanadium ..	51·00	69·2	=	3 × 23·066	Sb	= Na_3V
Xenon	130·2	Krypton . ..	82·92	47·28	=	2 × 23·64	Xe	= Na_2Kr
Niton	222·4	Xenon	130·2	92·2	=	4 × 23·05	Nt	= Na_4Xe
Mercury	200·6	Silver	107·88	92·72	=	4 × 23·18	Hg	= Na_4Ag
Columbium	93·5	Titanium ..	48·1	45·4	=	2 × 22·7	Cb	= Na_2Ti
Copper	63·57	Calcium . ..	40·07	23·50	=	1 × 23·50	Cu	= NaCa
Molybdenum ..	96·0	Aluminium ..	27·1	68·9	=	3 × 22·97	Mo	= Na_3Al
Gallium	69·9	Sodium . ..	23·00	46·9	=	2 × 23 45	Ga	= Na_3
Rhodium	102·9	Iron	55·84	47·06	=	2 × 23·53	Rh	= Na_2Fe
Ruthenium	101·7	Manganese ..	54·93	46·77	=	2 × 23·385	Ru	= Na_2Mn
Arsenic	74·96	Chromium .. (Not associated).	52·0	22·96	=	1 × 22·96		

TABLE IV.

Tin	119·0	Silicon	28·3	90·7	Sn	= ZrSi
Gold	197·2	Silver	107·88	89·32	Au	= ZrAg
Osmium	190·19	Ruthenium ..	101·7	89·2	Os	= ZrRu
Iridium	193·1	Rhodium ..	102·9	90·2	Ir	= ZrRh
Platinum	195·2	Palladium ..	106·7	88·5	Pt	= ZrPd
Radium	226·4	Barium	137·37	89·03	Ra	= ZrBa
Tungsten	184·0	Columbium ..	93·5	90·5	W	= ZrCb
Xenon	130·2	Argon	39·88	90·32	Xe	= ZrA

The second main principle, which remains to be further demonstrated, is "*sodium takes a prominent part in the formation of all elements of greater atomic weight than itself.*"

The constitution and structure of the elements, as here given, was obtained ten years ago, and so was not influenced in the slightest by the modern discoveries regarding the splitting up of the radioactive elements. Therefore these discoveries prove the correctness of this reasoning.

A STUDY OF VARIOUS SPECIES OF FUNGI.

By H. T. F. RHODES.

An analysis was made of four well-known species of fungi. The samples were obtained in October, November, and December. A short description of each variety will not be out of place.

The Common Earth Ball (Scleroderma vulgare).

The earth ball is small in the first stage, but is often 10 inches in circumference when full grown. Its outer surface is horny and of a dirty white colour, and the inner portion of a bluish grey. When this fungus begins to decay the inner portion becomes powdery, which is due to the formation of spores. It is not suitable for human consumption.

The Common Polyporus (Polyporus versicolor).

The above is too well known to require description. It grows on most dead trees.

The Edible Boletus.

[illegible] edible Boletus is a fungus about 3 inches in [illegible]. It has a brown cap and yellow gills. It is [illegible] gelatinous to the touch.

The Sulphur Tuft (Agaricus fascicularis).

The Sulphur Tuft is generally 2 inches in diameter, with a yellow cap and green gills. This fungus is one of the few poisonous varieties.

An outstanding feature of the analysis is the high percentage of nitrogen in these vegetables. This makes their food values an important factor. It is peculiar that the *Agaricus campestris* is, in the majority of cases, the only species of which use is made for human consumption, as there are many other species which are as palatable and in many cases quite as nutritious. But a still more important point is the use of the growths as feeding stuff for cattle. Many of the species which are unpalatable to human beings would probably be consumed quite readily by animals. It is a pity that year after year such large quantities of useful material should be allowed to rot. It is commonly supposed that the common mushroom is the only non-poisonous variety, but this is a fallacy, as certainly not more than 2 per cent of the English species are poisonous.

The general method of the analysis was as follows:—

The Moisture.

Ten to thirty grms. of the sample according to the species were dried in an air oven at 70° to 90° C., until they ceased to lose weight. The results were as follows:—

	Per cent.
Scleroderma vulgare	84·30
The edible Boletus	87·93
Agaricus fascicularis	88·14
Polyporus versicolor	54·31

These results must not be taken as absolutely indicative, as the moisture varies according to the size of the fungus, the moisture of the ground, and other conditions.

The Ash.

One to five grms. were burnt up in a platinum crucible and reduced to a perfect ash, then cooled under a desiccator and weighed:—

	Per cent.
Scleroderma vulgare	12·22
The edible Boletus	10·75
Agaricus fascicularis	6·60
Polyporus versicolor	5·92

The ashes were very hygroscopic, yellow while hot, green when cold.

The Crude Fibre.

Estimations of crude fibre were made by the acid and alkali method, 1 grm. of the fat-free sample being used in each case. The results were as follows:—

	Per cent.
Scleroderma vulgare	19·20
The edible Boletus	10·12
Agaricus fascicularis	10·33
Polyporus versicolor	20·41

It will be noticed that the crude fibre is very high in the first and last case and somewhat excessive in the other two. This is produced to some extent by the fibrous layer on the caps of the Boletus and *Agaricus fascicularis*, and also by the stem, but as these portions are both removed before consumption it is not of much importance. In the case of the *Polyporus versicolor*, the woody matter is not of such a superficial nature, as it partially partakes of the woody nature of the trees on which it grows. It may be broadly stated that on this account the *Polyporus* varieties are unsuitable for human or animal consumption. This statement applies in a somewhat modified degree to the *Scleroderma vulgare*, but much of the woody matter may be removed from this species by pealing off the outer husk.

The Nitrogen.

Estimations were made by Kjeldahl's process. One to two grms. were treated with 25 to 30 cc. of Nitrogen-free H_2SO_4, 10 grms. of potassium hydrogen sulphate were added, and after an hour a fragment of copper sulphate. The mixture was heated until the carbonaceous matter was destroyed. The acid was diluted with 250 cc. of distilled water, made alkaline with caustic potash, and steam distilled into 50 cc. of N/5 H_2SO_4. The results were as follows:—

	Per cent.
Scleroderma vulgare	5·29
The edible Boletus	7·02
Agaricus fascicularis	3·18
Polyporus versicolor	2·26

$\times 6{\cdot}25 =$ *Protein.*

Scleroderma vulgare	33·06
The edible Boletus	43·85
Agaricus fascicularis	19·87
Polyporus versicolor	14·12

The high percentage of protein will be noticed. It is of course of the highest importance from the point of view of nutriment.

The Fat.

One to two grms. of the finely ground sample were treated with petrol ether in a Soxhlet apparatus for 24 hours. The oils were very viscid at the ordinary temperature. In the case of the edible Boletus the oil was of a yellow colour, and in the other cases brown. In many cases the oils developed a most unpleasant odour if left exposed to the air for two or three days.

	Per cent.
Scleroderma vulgare	2·00
The edible Boletus	3·30
Agaricus fascicularis	3·82
Polyporus versicolor	1·23

Owing to a shortage of samples it was unfortunately impossible to make estimations of the carbohydrates, but more work will be in progress shortly in that direction.

The analysis was made on the dry samples in all cases. The above results compare very favourably with the analysis of dried lentils which appears in the "Scientists' Note-book and Diary for 1913," as follows:—

	Per cent.
Moisture	8·4
Protein	25·7
Fat	1·0
Ash	5·7
Carbohydrates	59·2

The lentil has a greater quantity of protein than the large majority of vegetables or fruit, and it will be noticed that its protein value is considerably lower than that of a dried sample of the edible Boletus. From the preceding analysis it is reasonable to assume that fungi can in many cases be used as a very satisfactory article of diet, a fact which until quite lately has been absolutely ignored, and is not at the present time by any means universally accepted. It has been suggested for use as food for cattle and other animals. It is not suggested that it should replace cotton and linseed cake, &c., but augment them.

A NEW STEAM GENERATOR.

By J. ALAN MURRAY, B.Sc.

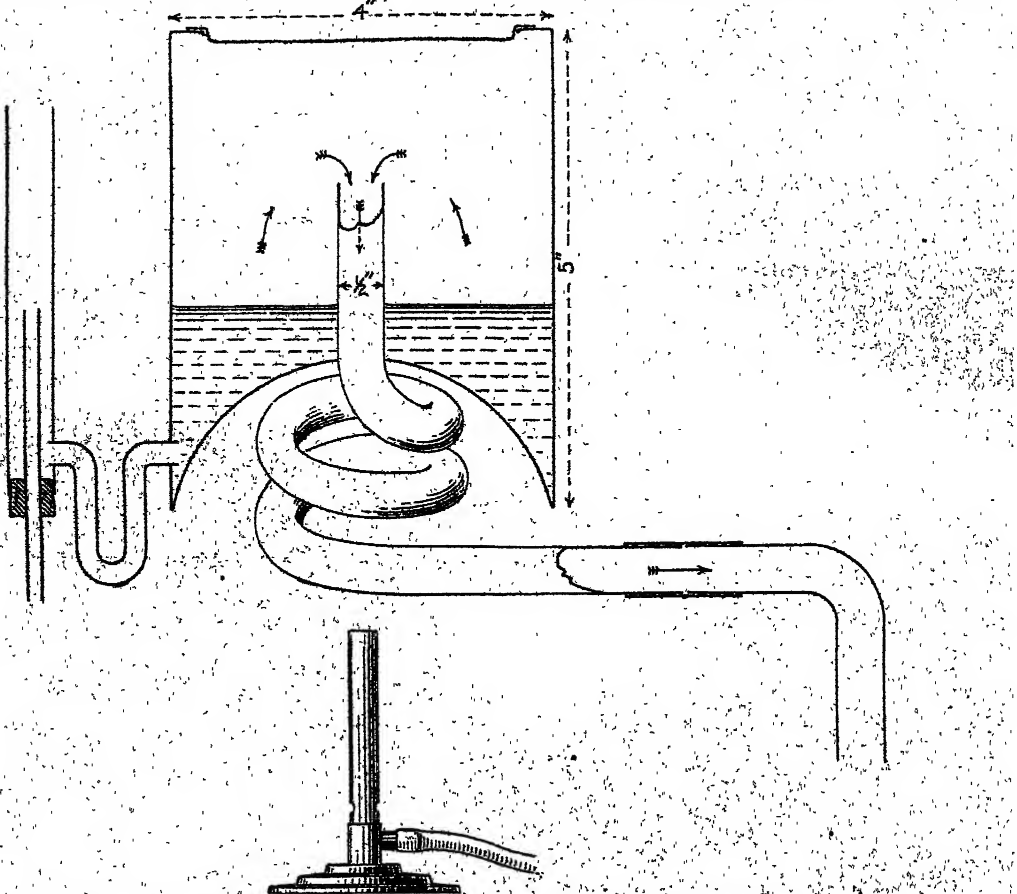
THE accompanying sketch shows the essential parts of a form of steam generator which has given very satisfactory results in my laboratory. The apparatus consists of a copper cylinder 5 inches high by 4 inches in diameter. It is fitted with an air-tight lid like that of a caustic soda tin, and the bottom is externally concave. A copper tube, ¼ inch in diameter, which passes through the bottom and projects to within about 1½ inches from the top, is coiled in two folds in the hollow outside the bottom. A space of about ¼ inch is left between the two folds of the coil, and also between the upper fold and the bottom of the cylinder to allow of the proper spread of the flame. The parts of the apparatus are brazed together.

Water is introduced into the cylinder and maintained at constant level by means of a side tube arrangement of the usual kind. The connecting tube is bent to prevent the too sudden access of cold water, which otherwise might cause the water to cease boiling. The steam which passes through the coil becomes superheated without any increase of pressure and may be used for many different purposes. The following results were obtained when the heat was supplied by means of an ordinary Bunsen burner, and the vapour was led into a small steam bath which measured 9×4½×4½ inches and weighed just under 1 lb.:—

0 minutes	Gas lighted.	
3 ,, ...	Water in cylinder boiled.	
7 ,, ...	Temperature in bath,	100° C.
11 ,, ...	,, ,,	120° C.
14 ,, ...	,, ,,	138—141° C.

The variation in the maximum temperature was attributed to the occasional inflow of cold water into the cylinder.

The rate of evaporation of water in basins placed on the bath was greatly accelerated. It was also found that water in a beaker covered with a watch-glass boiled when the vessel was completely immersed in the vapour, *i.e.*, hanging by the tip from the ring, but not if any considerable portion of it protruded. As the boiling takes place quietly and steadily this is a convenient method of heating liquids that are apt to froth or to bump and break the



(When in use the apparatus is supported on a tripod not shown in the diagram).

beakers. It has been successfully employed, for example, in the estimation of crude fibres.

The chief advantage of the apparatus, however, probably lies in the fact that it may be used to apply steam to baths, ovens, &c., made of zinc or tin instead of copper, and a considerable saving of cost can be thus effected. The apparatus itself can be made for about £1. It should also prove handy in laboratories that are so fortunate as to have steam "laid on," for it frequently happens that the supply fails at night or in vacation times. Of course one does not always want a temperature above 100° C., but the apparatus can be used as an auxiliary method of heating. All that is necessary is that the bath or oven should be provided with a tubular to fit the delivery pipe of the generator. This tubular can be closed with a cork when the generator is not in use. No solder or lute of any kind is required if the tubular fits the pipe fairly closely. One steam generator may, therefore, be used to heat several pieces of apparatus in turn. As it is small and easily disconnected it can be moved about the laboratory as required. To adapt it for these various purposes a collar, *i.e.*, a piece of copper tube of diameter slightly larger than the delivery pipe, is brazed on to the end of the latter, and another piece of the same size as the delivery pipe is bent at a right angle and fits into the collar. This is used as a connecting tube. It is not soldered into the collar, but merely fits in tightly, and so can be turned down or up or in a horizontal direction. By this means the generator can be readily accommodated to many different pieces of apparatus.

THE SCIENTIFIC WEEK.

(From Our Own Paris Correspondent).

Boron in the Human Organism.

There is no simple element that is not contained in the human organism. Quite recently M. Gabriel Bertrand, of the Pasteur Institute, has shown that our tissues contain boron. Dr. Roux now describes the method imagined by MM. Gabriel Bertrand and Agulhon to estimate the extraordinary small proportions of boron and boric acid that are normally found in all the parts of the animal and vegetable organism. These methods enable the estimation of the weights of metalloid as small as the half-thousandth of a milligrm. The method is based on the employment of little tests of turmeric. Vegetables contain from 100 to 1000 times more boron than that contained in animal tissues. The new method of analysis will facilitate the study of the accumulations of boron, and will allow it to be seen what is its physiological *rôle*.

The Formation of the Planetary System.

In 1880 the celebrated astronomer Payet searched how a spherical nebula, with a density increasing as far as the centre, could give birth to the primitive sun imagined by Laplace. In a communication made by M. Bigourdan to the Academy of Sciences, M. Emile Belot, Director of the State Manufactories, has taken up again the idea of Fayet, and has generalised it by applying it to the indefinite cylindrical layers in rotation, assembling whirlwind, or

vortex formations. It is then found that in such a spherical nubula there exist three remarkable cylindrical layers: one of which contains the maximum of centrifugal power; the third possesses the maximum tangential speed. The rays of these three layers are very much in the same relation to each other as the distance of Jupiter (the maximum mass) from Saturn (the mass of minimum density), and that which, in the solar system, separates the region of the planets with a direct rotation from those which move with a retrograde rotation.

The Frequency of Earthquakes.

The late English savant Milne, whose works on seismology are so well known, recently published a general catalogue of the destructive earthquakes registered since the beginning of this era. He found the principal elements of his work in the catalogues drawn up by Alexis Perrey, of Dijon. Without taking into account the little irregular shocks which are generally but a repercussion of intense and far off earthquakes, Milne reaches the total of 4000 seismic shocks. Up till the year 650 91 were noticed; that is to say, about 14 per century. From 650 to 1650 the total number of cataclysms reached 1099, or about a little more than one earthquake per year. From 1650 to 1840 the number of important shocks goes up to 11 per year. From 1840 to 1849 the annual average is 18, and it goes up to 31 for the period from 1850 to 1859. In these statistics there are numerous voids, but it may be supposed that from 1850 all the earthquakes of any importance are known. Now, from 1850 to 1898 no less than 1521 destructive earthquakes were counted; that is to say, about 31 per year, and the difference between the annual maximum does not exceed 2·8 per cent per annum of the total. The mundane seismic activity was then sensibly constant during the second half of the nineteenth century. The International Seismological Association, which every year publishes the statistics of earthquakes of a certain intensity, registers about 27,000 shocks for the years between 1900 and 1909. The number of earthquakes varies then from 250 to 300 per year, which is a considerable figure, seeing that the shocks that occur on the sea and in uninhabited regions are not taken into account.

Portable Wireless Telegraphy.

It is known that the Hertzian waves spread in all directions and to very great distances. Branley's coherer and different detectors enable them to be received easily. If one of these receptive apparatus is joined to a telephone, each signal of the wireless telegraphy produced by a spark more or less long is translated into the telephonic apparatus by a more or less prolonged top. But these instruments are rather cumbersome. An engineer, Justin Landry, has just presented before the Astronomical Society of France a pocket apparatus that is destined to receive wireless telegraphic signals. This tiny detector, formed by an inoxidisable crystal and a very hard steel point, is fixed to the bottom of a telephonic receptor. It has no attached coil, and in the majority of cases it is not necessary to have a hold on the ground. Trials have been made at the foot of the Eiffel Tower and as far as the furthest corners of France. The most diverse feelers have been employed. In Paris the mere contact of the isolated wire with any metallic body is sufficient, whether it be a simple curtain rod, or the gas and water pipes, or the framework of a motor-car or motor-bus. At distances varying from 40 to 50 kilometres from Paris, the roof-gutters, spouts, the railings, garden tools (such as spades), and, still better, steel frame umbrellas with wooden handles, enable one to assure an excellent reception of the signals from the Eiffel Tower. Further away, at a distance of 1000 kilometres telephonic wires or well arranged antennæ have allowed radiotelegrams to be very well received. M. Landry has signalled from antennæ or feelers that are always and everywhere to be found at hand; that is to say, trees. They have a considerable faculty of reception. At 80 kilometres from Paris a contact taken on a tree at a height of 2 or 3 metres with a pin or a gimlet pushed in to a certain depth, a hold on the ground managed by fixing the blade of a knife into the earth, have enabled meteorological despatches to be heard, and also the time signals and the radio-telegrams that the Eiffel Tower transmits every day all over the world. Atmospheric disturbances, such as storms, &c., also influence greatly the detectors. A characteristic noise of molten metal falling into water reveals these disturbances. It may be said that the lightning flashes are, as it were, heard long before they are seen. Colonel Renard has drawn attention to the services that the reception of meteorological radio telegrams might render to aeronauts and aviators.

Origin of Mildew in Plants.

Up till quite lately every one imagined that the rust or mildew of cereals and other plants was due to an exterior contamination caused by parasitic fungi belonging to the uredine group. However, in making wheat or corn germinate and grow in closed aseptic rooms, Prof. Eriksson, of Stockholm, announced fifteen years ago that the rust might appear at a given moment on the plants thus protected; whence it was naturally concluded that the parasite must already exist in the grain of corn itself. Divers experiments by M. Blaringhem, the results of which have been communicated to the Academy of Sciences by Prof. Guignard, have, on several points, confirmed the opinion expressed by Eriksson as to the origin of mildew. These experiments more especially concerned hollyhocks, the leaves of which are attacked by a special kind of rust. In taking all the possible and desirable precautions for this kind of experiment, M. Blaringhem has observed that if the seeds of this plant previously sterilised are put to germinate in places in which are also placed determined quantities of glucose and saccharose, the rust makes its appearance on the plantules, whereas it does not appear in the absence of these nutritive matters. The manifestation of the parasitary disease would then appear to be subordinate to certain conditions of environment. In any case there seems to be no doubt but that this rust is hereditary.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, December 4th, 1913.

Prof. W. H. Perkin, LL.D., F.R.S., President, in the Chair.

The President referred to the loss sustained by the Society through the death of James Tudor Cundall (Edinburgh) and Thomas Ebenezer Pye (Chichester).

The President announced that the Society had replenished its stock of apparatus and reagents for the use of Fellows making experiments at the meetings of the Society. Fellows can obtain a list of the apparatus and reagents by applying to the Assistant Secretary.

Certificates were read for the first time in favour of Messrs. Sydney George Clifford, 3, Norman Villas, East Dulwich, S.E.; Thomas Alexander Davidson, 57, Strathyre Avenue, Norbury; Thomas Eynon Davies, B.Sc., 25, Trevor Street, Aberdare; James Stanley Hale, Principe 4, Bilbao, Spain; Alfred John Leigh, B.Sc., Duff House, Banff; Archibald Macpherson, 51, Keir Street, Glasgow; Frederick Arthur Makin, The Nest, Taunton Road, Ashton-under-Lyne; Thomas Morris, 53, Poolstock, Wigan; Raymond William Nichols, Central Experimental Farm Ottawa, Canada; William Julian Odlum, B.A., Ardmore, Bray; Charles Alfred Stamp, Passey's House, Eltham; Eustace Ebenezer Turner, B.Sc., 5, Queen's Gate Villas, South Hackney, N.E.

Messrs. Harold King and W. B. Tuck were elected Scrutators, and a ballot for the election of Fellows was held. The following were subsequently declared as duly elected:—Parmanand Mewaram Advani, M.A., B.Sc.; Richard Watson Askew, B.A.; Sankar Rao B. Badami, M.A.; Alan Milsom Bailey; Stanley Charles Bate, B.Sc.; Alan Hamilton Bateman; Charles Maurice Berlein, B.A.; Arthur Bicknell, B.Sc.; Augustus Pearce Llewellyn Blaxter, B.A.; Adhor Krishna Bose; Arthur Bramley, B.Sc.; Arthur Joseph Brearley, B.A.; George Bernard Butler; Bertram Campbell, B.Sc.; Norman Phillips Campbell, B.A.; Frederick George Carter; Santi Pada Chowdry; Francis William Clark; Herbert Stoddard Coleman; Thomas James Drakeley, B.Sc.; Mohamed Shams Eldin, B.Sc.; Cyril Duncan Fuller; Charles John Dickenson Gair; Stanton Gibson, B.Sc.; Richard Hargreaves, B.A.; Alexander Houghton Hay; George Alfred Hebden; Richard Pendarves Hodges; William Francis Holleley; Charles Huxtable; Alexander Hynd, M.A., B.Sc.; William Johnson, B.Sc.; Harold Bramfield Jones; Ghulam Rasul Khan, B.Sc.; Sidney Oliver Leivesley; William John Lewis; Percival James Lycett; Frank Clifford Marchant; Kunerji Gosai Naik, M.A., B.Sc.; John Allen Nichols; John Thomas Pattison; Wilfred Roberts Powell, B.A.; Henry Edward Findlater Pracy; Benedict Hugh Rolls, M.A.; Philip Howard Stott; John McArthur Stuart; John Algernon Lacy Sutcliffe; Harold Frank Tayler; Robert Tennant; Henry Walker; Bertie Mandel Welch; Henry Wood.

Of the following papers those marked * were read:—

*305. "*The Action of Sulphuric Acid on Copper.*" By (the late) JAMES TUDOR CUNDALL.

It is commonly supposed that the mutual action of copper and sulphuric acid may be represented by the production first of cupric sulphate and nascent hydrogen, which latter produces more sulphuric acid and from it sulphur dioxide.

The present investigation shows that cuprous sulphate, rather than cupric sulphate, is one of the primary products, as may easily be tested by pouring off the sulphuric acid at any stage of the reaction through a Gooch filter into water, when a precipitate of finely divided copper is produced. This result is best obtained when the sulphuric acid is slightly diluted with water, for when hot or concentrated acid is used, the cuprous sulphate acts on the acid almost as soon as formed, giving cuprous sulphide and cupric sulphate. This last action also takes place, but more slowly, with cooler acid.

The cuprous sulphide then, as Pickering found, becomes oxidised to cupric sulphide and cupric sulphate with evolution of sulphur dioxide, and thereafter the cupric sulphide gives the sulphate, with a further evolution of gas.

*306. "*Synthesis of Polypeptides from the Higher Fatty Acids.*" By ARTHUR HOPWOOD.

Although so many polypeptides have been prepared lately, only one has been obtained from the higher fatty acids. The author has therefore synthesised several dipeptides from palmitic and stearic acids, so that their properties could be ascertained and compared with those of the degradation products of the proteins.

α-Bromopalmityl chloride, $C_{15}H_{30}Br\cdot COCl$, prepared from α-bromopalmitic acid and thionyl chloride, is a colourless oil, which crystallises on cooling, and boils with decomposition at about 215°/20 mm.

α-Bromopalmitylglycine, $C_{15}H_{30}Br\cdot CO\cdot NH\cdot CH_2\cdot CO_2H$, prepared by condensing α-bromopalmityl chloride with glycine, crystallises in colourless plates, melting at 118—121°.

α-Aminopalmitylglycine,—

$$NH_2\cdot C_{15}H_{30}\cdot CO\cdot NH\cdot CH_2\cdot CO_2H,$$

prepared by heating α-bromopalmitylglycine with ammonia, crystallises in colourless hexagonal plates, melting and decomposing at 222—224°.

Similar dipeptides have been prepared by coupling α-bromopalmityl or α-bromostearyl chloride with alanine or leucine, and heating the products with ammonia. Isomerides of these dipeptides have also been prepared by the action of ammonia on the products obtained by condensing α-bromoacetyl, α-bromopropionyl, or α bromo*iso*hexoyl chloride with α-aminopalmitic or α-aminostearic acid.

The dipeptides derived from palmitic and stearic acids are tasteless, or slightly bitter, crystalline solids melting and decomposing at above 200°. They are insoluble in water, alcohol, ether, or benzene, but dissolve in hot dilute mineral acids or alkali hydroxides. They form characteristic crystalline compounds with β-naphthalenesulphonyl chloride, and, like the natural proteins, the dipeptides give white amorphous precipitates with phosphotungstic acid.

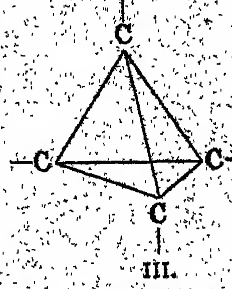
*307. "*A New Series of Ring Compounds.*" (Preliminary Note). By RICHARD MOORE BEESLEY and JOSEPH FIELD THORPE.

The fact that the ethyl ester of labile β-methylglutaconic acid, which can be readily obtained from ethyl acetoacetate (*Trans.*, 1912, ci., 1565), condenses with the sodium compound of ethyl cyanoacetate, yielding the cyano-ester (I.), and that from this ester an almost quantitative yield of the tricarboxylic acid (II.) can be obtained on hydrolysis, has led to an investigation in which the possibility of the existence of "enclosed" or "caged" carbon rings has been studied.

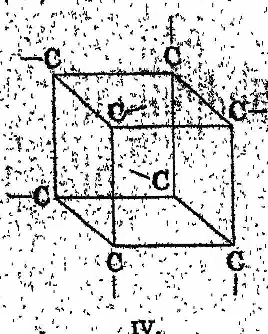
$$CH_3\cdot C\begin{cases}CH_2\cdot CO_2Et\\ CH(CN)\cdot CO_2Et\\ CH_2\cdot CO_2Et\end{cases} \qquad CH_3\cdot C\begin{cases}CH_2\cdot CO_2H\\ CH_2\cdot CO_2H\\ CH_2\cdot CO_2H\end{cases}$$

I. M. p. 30°. II. M. p. 179°.

It is evident that the simplest type of such a series would be the enclosed four-carbon ring in which the carbon atoms occupy the four points of a tetrahedron, as in formula (III.), whilst another type would be the "caged" cube as in formula (IV.).



III.

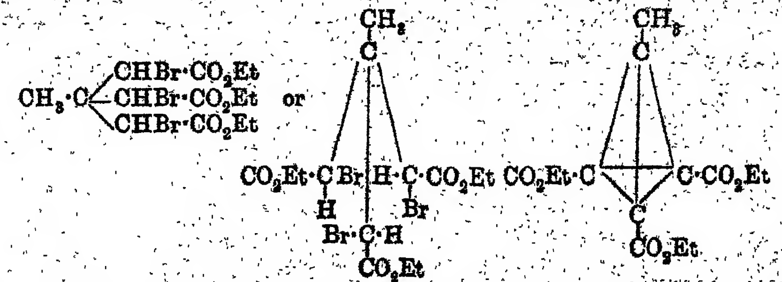


IV.

It is well known that the esters of the bromoglutaric acids eliminate hydrogen bromide and pass into derivatives of *cyclo*propane, and it therefore follows that if this reaction could be applied to the tribromo-ester (V.), which can be prepared by the bromination of the acid (II.), that ring-formation would ensue in accordance with the accompanying scheme (V.) and (VI.).

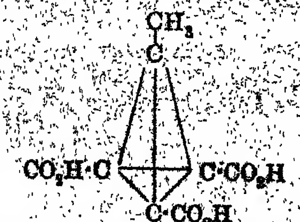
Many difficulties were experienced in attempting to accomplish this change, because it was found that all the usual reagents, employed for the purpose of eliminating hydrogen bromide, led to the production of the corresponding lactones. Ultimately a reaction was discovered, which has since been found to succeed in a number of other cases, and seems to favour the formation of the carbon ring from compounds of this character. The reaction is carried out by adding the bromo-ester to a very concentrated aqueous solution of potassium hydroxide at 130°. The reaction is very violent, but the more violent it is the better is the yield of the ring compound.

By the aid of this reaction, the tribromo-ester (V.) has been converted into a tricarboxylic acid having the formula



(V.) (VI.)

$C_8H_6O_6$, which has all the properties of the "caged" ring tricarboxylic acid:—



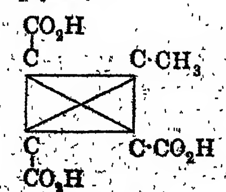
(M. p. 187°.)

The acid is a remarkably stable substance, and does not decolorise alkaline permanganate in the cold; it is not attacked by bromine at the ordinary temperature. It yields methylsuccinic acid when oxidised by hot alkaline permanganate.

DISCUSSION.

In reply to Prof. Armstrong, Dr. THORPE said that so soon as larger quantities of material had been prepared it was his intention to study the action of hydrogen bromide, but it was necessary in order thoroughly to investigate the products of this reaction that considerable quantities of material should be available.

In reply to Sir W. Ramsay, he said that the formula of the "caged" ring compound could only be expressed in the plane of the paper by:—



representing the compound as a derivative of *cyclo*butane, which it certainly was not.

*308. "*Organic Derivatives of Silicon.* Part XX. *Some Condensation Products of Dibenzylsilicanediol.*" By ROBERT ROBISON and FREDERIC STANLEY KIPPING.

The two condensation products of dibenzylsilicanediol, namely, anhydrobisdibenzylsilicanediol and trianhydrotrisdibenzylsilicanediol (Robison and Kipping, *Trans.*, 1912, ci., 2142), have been further studied in order to ascertain the conditions under which they are formed.

A further condensation product, namely, *dianhydrotrisdibenzylsilicanediol*,—

$$HO{\cdot}Si(CH_2Ph)_2{\cdot}O{\cdot}Si(CH_2Ph)_2{\cdot}O{\cdot}Si(CH_2Ph)_2{\cdot}OH,$$

has also been obtained by the partial hydrolysis of trianhydrotrisdibenzylsilicanediol with potassium hydroxide, and with hydrochloric acid, in a suitable solvent. This compound crystallises in massive prisms, melting at 82°, and is analogous to dianhydrotrisdiphenylsilicanediol; it is readily transformed into trianhydrotrisdiphenylsilicanediol when it is treated with hydrogen chloride in alcoholic solution, the following reversible reaction taking place—

$$Si(CH_2Ph)_2{<}^{O\cdot Si(CH_2Ph)_2\cdot OH}_{O\cdot Si(CH_2Ph)_2\cdot OH} \rightleftharpoons Si(CH_2Ph)_2{<}^{O\cdot Si(CH_2Ph)_2}_{O\cdot Si(CH_2Ph)_2}{>}O + H_2O.$$

*309. "*The Rotatory Dispersive Power of Organic Compounds.* Part V. *A Comparison of the Optical and Magnetic Rotatory Dispersions in some Optically Active Liquids.*" By THOMAS MARTIN LOWRY, ROBERT HOWSON PICKARD, and JOSEPH KENYON.

After examining thirty-four optically active liquids, only two cases have been found in which the optical and magnetic rotatory dispersions are approximately equal; even this equality is fortuitous, as it does not appear in the next homologues. Wiedemann's law, which applies exactly in the case of quartz, does not therefore hold good for optically active liquids.

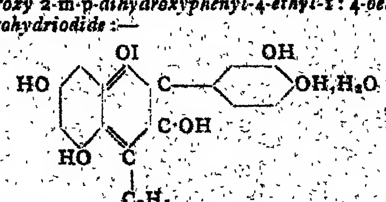
310. "*A Relation between Chemical Constitution and Depth of Colour of Dyes.*" By EDWIN ROY WATSON.

The theory is put forward that those dyes which are quinonoid in all possible tautomeric forms exhibit a deep colour, however simple the molecule may be. On the other hand, if there is the possibility of the molecule existing in a non-quinonoid form, it may not attain a deep colour, although the molecular complexity may be very considerable. A survey of all the better known dye-stuffs fully bears out this theory, and it explains remarkable differences in depths of colour between dyes of very similar constitution. A permanent quinonoid structure alone is not sufficient, for example, dihydroxy-*p*-benzoquinone; the substance must be capable of tautomerising from one quinonoid arrangement to another.

The theory has been fully borne out by the preparation of dyes of deep colour from quercetin.

311. "*Dyes Derived from Quercetin.*" By EDWIN ROY WATSON and KUMUD BEHARI SEN.

By the action of magnesium ethyl iodide on quercetin pentaethyl ether, there is obtained 3 : 5 : 7-*triethoxy*-2-m-p-*diethoxyphenyl-4-ethyl-1 : 4-benzopyran anhydrohydriodide*, which, on de-ethylation, yields 3 : 5 : 7-*trihydroxy* 2-m-p-*dihydroxyphenyl-4-ethyl-1 : 4-benzopyran anhydrohydriodide* :—



this dyes wool violet (on alum and chrome) and crimson (on tin).

3 : 5-*Dihydroxy-7-keto-4-dimethylaminophenyl*-2-m-p *dihydroxyphenyl-1 : 4-benzopyran*, obtained from quercetin

by the action of dimethylaniline in the presence of phosphoryl chloride, dyes wool in slaty-blue shades on all mordants. 3 : 4 : 5 : 7-*Tetrahydroxy*-2-m-p-*dihydroxyphenyl* 1 : 4-*benzopyran*, prepared by the reduction of quercetin by sodium amalgam in alcoholic hydrochloric acid solution, dissolves in alcohol with a magenta colour, and in potassium hydroxide to a green solution, but is very readily oxidised to quercetin.

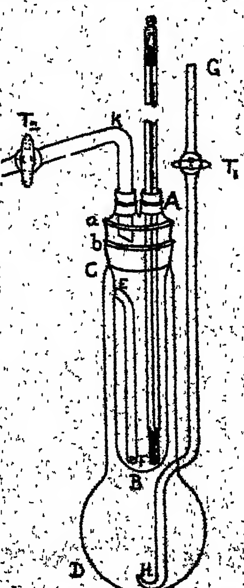
Several other derivatives of quercetin and 2-phenyl-1 : 4-benzopyran were also prepared.

312. "*An Improved Apparatus for the Determination of Molecular Weight by the Landsberger-Sakurai Method.*" By William Ernest Stephen Turner and Cornelius Theodore Pollard.

The great convenience of the Landsberger-Sakurai method of determining molecular weights, especially as a time-saver (see Note 1), has led to its adoption in principle in a number of pieces of apparatus devised by subsequent investigators. Most of these forms, however, are unsuitable for accurate work, and in a paper which discussed the various sources of error in the Landsberger-Sakurai method (Turner, *Trans.*, 1910, xcvii., 1184) an apparatus was described which enabled rapid and accurate measurements to be undertaken.

During the course of some three years' work with this apparatus, several improvements have suggested themselves, and have been collected in the new form figured below.

The most important alteration of the original is the use of the boiler as the constant temperature jacket (see Note



2). For one of the disadvantages of the Landsberger and Sakurai forms of apparatus is that the molecular-weight tube fills so readily as to make it difficult, with easily condensable vapours, to obtain more than three or four readings in a series. By using the boiler as outer jacket and making the entrance for the vapour stream high up in the molecular-weight tube, the cooler solvent or solution in the tube is heated considerably before the entrance of vapour, and the amount of condensation thus diminished.

The molecular-weight tube AB, 17·5 cm. in length, 2·8 cm. diameter in the main portion, and 3·5 cm. at the mouth, carries a ground-glass stopper with two tubulures, fitting flush with the mouth of the tube at *a*. To the solvent or solution under measurement, vapour is admitted through two perforations at the bottom of the tube EF, the entrance E being 12 cm. from the lower end of the molecular-weight tube. The outer jacket CD, of approximately 5 cm. diameter in the cylindrical portion, fits the molecular-weight tube at a second ground joint at *b*, and carries a safety-tube GH, provided with a tap T_1. Although shown in one piece, the tube sealed into the boiler reached only the level of the tubulated stopper, and the tap was connected by rubber tubing, the ends of the tubes being in contact. Whilst a determination is in progress, T_1 is usually closed in order to drive a steady stream of vapour through E, but when the molecular-weight tube has been removed for weighing, a cork is inserted in the mouth of the boiler, and T_1 is opened to admit dry air, drawn in through drying tubes connected at G. Hygroscopic solvents are thus protected.

Vapour escapes by the tube K, of length as short as possible, connexion with the condenser being made at a third ground joint, so that the molecular-weight tube, together with the thermometer and escape tube, can be lifted away bodily for weighing, during which process the tap T_2 is closed. A small cork may be inserted at E if desirable, and complete protection from moist air thus secured.

Of other points it may be remarked that the molecular-weight tube is graduated with marks 2 mm. apart to assist in determining the correction for the use of boiling-point due to increasing head of liquid (alternatively the graduation may be in cc.); that the thermometer used is one of the Beckmann type specially made by Baumbach, of Manchester; and that it is advantageous to protect the cylindrical portion of the outer jacket by two or three thicknesses of asbestos paper, and so diminish the loss of heat by radiation.

The following results were obtained during the course of little more than an hour from the time of setting up the apparatus:—

Pyrogallol in Ethyl Alcohol. $C_6H_3(OH)_3 = 126·0$.
(Weight of Solute, 0·8090 grm.).

Weight of solvent. Grms.	Δ°.	M.W.
9·69	0·773	124·9
11·90	0·625	125·7
14·31	0·530	123·7
16·71	0·444	126·1
19·17	0·399	124·0
21·92	0·332	128·3
23·96	0·277	128·4
Mean		125·9

Several readings did not mark the limit of the capabilities of the apparatus with this solvent, and as no more than five could, as a rule, be obtained with the earlier form, the efficiency of the new apparatus is considerably greater. Ethyl ether, carbon disulphide, and water are easier to handle than alcohol, and with them quite a long series of readings is obtainable. When, however, the boiling-point of the solvent exceeds 100°, the number of readings becomes less, so that with amyl alcohol, for example, only four readings were obtained. Above 150° the apparatus may conveniently be employed only in measurements where it is sufficiently accurate to assume that the volume of the solution is the volume of the solvent; for in such a case it is unnecessary to detach the molecular-weight tube, thus avoiding the inconvenience of handling it at a high temperature.

For a discussion of the details requiring attention and the corrections to be applied in accurate work, reference should be made to the previous paper on the subject.

Note 1.—Besides saving time, the rapidity of the process permits the investigation of substances which would decompose during the prolonged boiling involved in the ordinary Beckmann method. Such substances are triethylsulphonium salts (see Turner, *Trans.*, 1911, xcix., 880) and amylamine hydrochloride (Turner, *loc. cit.*; compare Hantzch and Hofmann, *Ber.*, 1911, xliv., 1776).

Note 2.—In much the same way as used by McCoy (*Amer. Chem. Journ.*, 1900, xxiii., 353) and Ludlam (*Trans.*, 1902, lxxxi., 1193).

(We are indebted to the Chemical Society for permission to reproduce the accompanying woodcut.)

(To be continued).

SOCIETY OF CHEMICAL INDUSTRY.
(LONDON SECTION).

Ordinary Meeting, January 5th, 1914.

Dr. W. R. E. HODGKINSON in the Chair.

THE following papers were read and discussed:—

"*Viscosity of Oils.*" By J. L. STREVENS.

The author, after emphasising the importance of the determination of absolute viscosity and its relation to temperature for any particular lubricant, proceeds to correct certain figures previously published by Dunstan and himself on the basis of the more correct case for the viscosity of phenol at various temperatures due to Dunstan and Thole.

1. Increase of molecular weight favours increase of Zt, *e.g.*, rape oil (trieninm) > olive oil (triolein).

2. Hydroxyl formation favours increased Zt, *e.g.*, castor oils and the blown oils.

3. Solution of solid bodies in oils (*e.g.*, "soaping") tends to a high viscosity temperature coefficient.

4. Combined high molecular weight and conjugated double bonds mean a high Zt, *e.g.*, tung oil.

5. Unsaturation tends to lower the viscosity, and broadly the greater the iodine value the lower Zt, *e.g.*, linseed and perialla oils less than nut or olive oil.

Experimental results are given and the recent work of Higgins at the National Physical Laboratory is referred to.

"*Oxygen Content of the Gases from Roasting Pyrites.*" By LEWIS T. WRIGHT.

The author calls attention to the discussion that arose forty years ago between Scheurer-Kestner and Friedr. Bode on the deficiency noted by the former in the oxygen of the gases from roasting pyrites if the pyrites were fully oxidised according to the equation $2FeS_2 + 11O = Fe_2O_3 + 4SO_2$.

The matter was not satisfactorily cleared up by this discussion in which Lunge took part, because the amount of SO_3 formed either free or as metallic sulphate in the cinder did not explain the full extent of the deficiency. Lunge suggested there might also be some error in the absorption of the oxygen by the pyrogallate in the course of the gas analysis. The author, on examining a number of analyses of "burner" gas from various sources, noticed that the oxygen "deficiency" is the greater the greater dilution of the gas, and this suggests that there is, in addition to the well-known production of SO_3 and metallic sulphates, some other cause, such as a constant error in the analyses which influences these. In any case the evidence of these gas analyses shows that the manner in which the oxygen is disposed of would prevent the "burner" gas from containing more than about 12 per cent of SO_2 as a maximum when all the oxygen of the air applied was used up, and the author states that his various attempts to obtain more than this in practice by keeping burner gas long in contact with incandescent pyrites have failed.

"*Electrical Conductivity of Milk during the Concentration, with Suggestions for a Practical Method of Determining the End-point in the Manufacture of Sweetened Condensed Milk.*" By L. C. JACKSON, LESLIE MCNAB, and A. C. H. ROTHERA.

The authors have studied the variation of the electrical conductivity of milk during the process of concentration. They find that although the measurement of electrical conductivity is of no value in determining the degree of concentration of a separated unsweetened milk, it can be made the basis of a working process for watching the concentration of sweetened whole milk.

An ingenious device in which the resistance of sweetened milk in the vacuum pan is compared with that of an approved sample of condensed milk maintained at exactly the sample temperature is described.

Numerous experiments on which the authors base their method are described in the paper.

"*Monazite from some New Localities.*" By SYDNEY J. JOHNSTONE.

In this paper are given the results obtained and the methods of analysis employed in the examination of twenty-one samples of pure monazite from new localities in Ceylon, Travancore, Nyassaland, Malaya, Northern and Southern Nigeria. The results show that wide variation may occur in the quantity of thoria present in samples; notable amongst these are ranges shown by those from Ceylon whose thoria percentage varies from 9·5 to 28·2, from Malaya 3·4 to 9·4, and from Northern Nigeria 2·3 to 8·0.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clvii., No. 20, November 17, 1913.

Thermochemistry of Acetylenic Compounds. — Charles Moureu and Emile André.—The heat of hydrogenation of acetylenic compounds is considerable. It is of the order of 80 cal. in the fatty series and decidedly less in the aromatic series. The fixation of the first half of the hydrogen (2 atoms) to give an ethylenic compound generally liberates more than half of the heat disengaged in the complete saturation. The excess of energy of the triple bond over the simple bond is about 70 cals. in the first members of the series. The fixation of water by an acetylenic hydrocarbon, with formation of a ketone, liberates a quantity of heat of the order of 40 cals.

Influence of Silicon on the Solubility of Carbon in Iron. — Georges Charpy and André Cornu. — Silicon gradually diminishes the solubility of carbon in iron until it becomes practically equal to zero at 900°, when the amount of silicon present exceeds 4 per cent. It also vanishes at 1000°, when the percentage of silicon exceeds 7.

Complex Salts of Uranium.—Paul Pascal.—When uranyl pyrophosphate is dissolved in a solution of the sodium salt the solidification point rises, reaches a maximum, when the two salts are present in the proportion $3P_2O_7Na_4 : P_2O_7(UO_2)_2$, and then descends to a minimum at $2P_2O_7Na_4 : P_2O_7(UO_2)_2$. Up to this point the solution exhibits none of the properties of uranyl salts. When the solution is saturated with uranyl pyrophosphate the ratio is $P_2O_8Na_4 : P_2O_7(UO_2)_2$, and the liquid then exhibits the properties of a strongly diluted uranyl salt. The intermediate pyrophosphate must be regarded as a normal uranyl pyrophosphate of formula $[(UO_2)_2(P_2O_7)_4]Na_8$. The evaporation of its solution gives a gummy mass which treatment with methyl alcohol transforms into a hygroscopic powder, $[(UO_2)_2(P_2O_7)_3]Na_8 + 6H_2O$ at 15° ($+ 4H_2O$ at 100°). The saturated solution of uranyl pyrophosphate contains the uranyl sodium salt of the acid. It is a yellow unstable powder, readily transformed into the isomeric double pyrophosphate $P_2O_7(UO)_2Na_2.H_2O$. All these complex salts are dissociated when their solutions are heated. Alcoholic solutions of potassium cyanate and uranyl nitrate when mixed give a yellow microcrystalline precipitate of formula $[UO_2(CNO)_4]K_2$. This complex salt is analogous to the anhydrous cobaltocyanate, $Co(CNO)_4K_2$. In water it gradually dissociates, giving an orange double salt, $2UO_2(CNO)_2 + KCNO$. An excess of alkaline cyanate causes the formation of the salt $UO_2(CNO)_2 + KCNO$, while

an excess of uranyl salt precipitates $UO_2(CNO)_2$. These two examples are not isolated, and according to the acid radicle introduced the uranyl complex can have either of the following constitutions:—$[UO_2X_5]M_4$ or $[UO_2X_4]M_2$. The first type is always very stable; it resists hydrolysis and the uranium reactions are completely masked in it. The second type in dilute solution behaves like a double salt, and an enormous excess of alkaline salt is necessary to prevent dissociation.

Action of Carbon Dioxide on Boron Sulphide.—N. D. Costeanu.—Carbon dioxide acts on boron sulphide in the same way as on silicon sulphide, transforming it into boric anhydride with formation of carbon monoxide and sulphur:— $B_2S_3+3CO_2=B_2O_3+3CO+3S$. The reaction begins at 300°, but the change is not rapid at this temperature. It is accelerated by raising the temperature and prolonging the heating, but it never occurs very quickly owing to the formation of a protective layer of B_2O_3 on the surface of the sulphide.

Colours of Glasses containing Copper.—Albert Granger.—Glasses are coloured blue by copper when only a very small amount is present. With 0·05 CuO for a molecule of base a very satisfactory blue coloration is obtained. On increasing the amount of copper the glass shows a tendency to turn green, and this tendency is increased by the addition of alumina or boric anhydride. Glasses containing boric anhydride have a very dark colour; when they are some millimetres thick they are nearly opaque. The most important factor in the preparation of a blue glass is a convenient proportion between the bases; the acidity of the glass has no effect on the tint. Certain glasses show a tendency to deposit copper when they are quickly cooled.

Products of Concentration of Nitrated Benzyl Chlorides with Acetylacetone, Methylacetylacetone, and Cyanacetic Ethers.—H. Mech.—When di-*p*-nitrobenzylacetylacetone is reduced with zinc and hydrochloric acid the product is di-*p*-aminobenzylacetylacetone. *p*-Nitrobenzyl chloride reacts with methylacetylacetone to give methyl-*p*-nitrophenylbutanone. Di-*p*-nitrobenzylcyanacetate of methyl is readily obtained by the action of nitrated chlorides of benzyl upon a solution in methyl alcohol of sodium methyl cyanacetate.

MISCELLANEOUS.

Royal Institution.—On Tuesday next, January 20, at 3 o'clock, Prof. W. Bateson will deliver the first of a course of six lectures at the Royal Institution on "Animals and Plants under Domestication"; on Thursday, Jan. 22, Mr. W. McDougall, M.A., F.R.S., begins a course of two lectures on "The Mind of Savage Man"; and on Saturday, Jan. 24, Prof. Frederick Corder will give the first of three lectures, with musical illustrations, on "Neglected Musical Composers—(1) Ludwig Spohr, (2) Henry Bishop, (3) Joachim Raff." The Friday Evening Discourse on January 23 will be delivered by Prof. Sir James Dewar, on "The Coming of Age of the Vacuum Flask"; and on Jan. 30, by Mr. H. Wickham Steed, on "The Foundations of Diplomacy."

Mining Exhibition.—The Third Annual Mining Exhibition under the auspices of the Chemical, Metallurgical, and Mining Society of South Africa, will be held in the Volunteer Drill Hall, Twist Street, Johannesburg. The Exhibition will open on Tuesday, May 19, and will close on Friday, May 29, 1914. The scope of the Exhibition will be on much the same lines as in previous years, *i.e.*, chemical, metallurgical, and mining apparatus and device for laboratories, works, and mines; models, working or otherwise, of apparatus for similar purposes; plans, diagrams, &c., of mines, works, plants, machinery; and apparatus; safety and rescue and other ambulance apparatus and appliances; and specimens of crude and manufactured mineral or other natural products of South Africa. The Exhibition is primarily for the benefit and information of those engaged and interested in mining work, and to give those in search of mineral products an opportunity of ascertaining where these products may be obtained. Commercial firms, for whom a limited space will be provided, desirous of exhibiting machinery, apparatus, natural products, &c., will be charged for the space occupied at from 5s. to 10s. per square foot, according to position, and whether stands are provided or not. Those desirous of engaging space provisionally are requested to specify their requirements with the least possible delay to the undersigned. The usual arrangements for exhibitions with regard to Customs duties and railway rates will be made.—Fred Rowland, Secretary, South African School of Mines and Technology Building, Eloff Street, Johannesburg.

MEETINGS FOR THE WEEK.

Monday, 19th.—Royal Society of Arts, 8. (Cantor Lecture). "The Relation of Industry to Art," by Sir Charles Waldstein, Litt.D., Ph.D.

Tuesday, 20th.—Royal Institution, 3. "Animals and Plants under Domestication," by Prof. W. Bateson, F.R.S., &c.

Wednesday, 21st.—Royal Society of Arts, 8. "The Modern Poster, its Essentials and Significance," by W. S. Rogers.

—— Microscopical, 8. Presidential Address by Prof. G. Sims Woodhead, "The Microscope and Medicine."

Thursday, 22nd.—Royal Institution, 3. "The Mind of Savage Man," by W. McDougall, F.R.S.

—— Royal Society. "Heat Production Associated with Muscular Work" (a Note on Prof. Macdonald's Paper, *Proc. R. S.*, B, lxxxvii.), by R. T. Glazebrook and D. W. Dye. "Chemical Interpretation of some Mendelian Factors for Flower Colour," by M. Wheldale and H. L. Bassett. "Determination of the Minimum Lethal Dose of various Toxic Substances and its Relationship to the Body Weight in Warm-blooded Animals, together with considerations bearing on the Dosage of Drugs" by G. Dreyer and E. W. A. Walker. "Experiments on the Restoration of Paralysed Muscles by means of Nerve Anastomosis—Part II., Anastomosis of the Nerve supplying Limb Muscles," by R. Kennedy "Variations in the Sex Ratio of *Mus rattus* following an Unusual Mortality of Adult Females, based on an Analysis of Weight Frequency Distributions," by F. N. White.

—— Chemical, 8.30. "Crystals of Organic Compounds Coloured Blue by Iodine," by G. Barger and W. W. Starling "Preparation and Properties of Pure Formic Acid" and "Mutual Solubility of Formic Acid and Benzene and the System Benzene—Formic Acid—Water," by A. J. Ewins. "Loose Compounds of Cholesterol with Barium Methoxide," by E. Newbery. "Vapour Pressure of Nitrogen Peroxide," by A. C. G. Egerton. "Organic Derivatives of Silicon—Part XXII., The Siliconic Acids" by C. J. Meads and F. S. Kipping. "Condensation of Glutaconic Ester," by R. Curtis and J. Kenner. "*β*-Hydrindamine," by J. Kenner and A. M. Mathews. "Reactions of Isoamarine, with Notes on *d*- and *l*-Isoamarine Sulphates and Amended Values of the Rotatory Power of *d*- and *l*-Isoamarine," by H. L. Snape. "Constituents of *Solanum angustifolium*" and "Solangustine, a New Gluco-alkaloid," by F. Tutin and H. W. B. Clewer. "Studies of the Constitution of Soap Solutions—the Electrical Conductivity of Potassium Salts of Fatty Acids," by H. M. Bunbury and H. E. Martin. "Occurrence of three Partially Miscible Liquids in a Four-component System, Ether—Water—Potassium Iodide—Mercuric Iodide, at 20°," by A. C. Dunningham. "Inversion of Cane-sugar by Acids in Water-Alcohol Solutions," by C. J. Burrows.

Friday, 23rd.—Royal Institution, 3. "The Coming of Age of the Vacuum Flask,'" by Prof. Sir James Dewar, F.R.S., &c.

—— Physical, 5. "Some Characteristic Curves and Sensitiveness Tests of Crystal and other Detectors," by P. R. Coursey. Exhibition of Water Model of the Musical Arc, by W. Duddell. "Experiments with Liquid Drops and Globules" by C. R. Darling. Note on Aberration in a Dispersive Medium and Airy's Experiment," by J. Walker.

Saturday, 24th.—Royal Institution, 3. "Neglected Musical Composers," by Prof. F. Corder.

THE CHEMICAL NEWS.

VOL. CIX., No. 2826.

THE ESTIMATION OF ALCOHOL IN BEER BY MEANS OF MALLIGAND'S EBULLIOSCOPE.

By JOHN CANNELL CAIN.

IN view of the fact that the methods usually employed for the estimation of alcohol in beer involve the use of more or less complicated chemical apparatus, including often a delicate balance, and the employment of gas and water, it is rather remarkable that determinations with the simple apparatus invented by Vidal and improved by Malligand and Mlle. E. Brossard-Vidal (*Comptes Rendus*, 1874, lxxviii., 1470) seem hitherto not to have been published in this country.

This is the more surprising as it has been abundantly proved that the apparatus furnishes very exact results, and it combines the great advantage that a determination can be carried out in a few minutes, and no chemical appliances are required for its use. Thus Dumas, Desain, and Thenard (*Comptes Rendus*, 1875, lxxx., 1114) presented a report to the French Academy in which they showed that by means of the ebullioscope the estimation of alcohol in wine could be carried out with great exactness, and Griessmayer (*Dingler's Polytech. Journ.*, 1875, ccxviii., 262) proved the same in the case of German beers. Further, in a long report to the Royal Finance Department, Kristiania, Waage ("Ebullioskopet og dets Anwendelse ved Beskatning af Ol efter dets Alkoholgehalt"; see also *Zeit. Anal. Chem.*, 1879, xviii., 417) made an exhaustive examination of this method, and demonstrated that it yielded accurate results, which he illustrated by comparative analyses of a large number of Scandinavian beers.

It therefore appeared to be of interest to apply this method of estimating alcohol to the case of English beers, and the results confirm those of the authors already mentioned in that the method is shown to be exact, rapid, and capable of being used by anyone who can read a thermometer.

The principle of the method depends of course on the fact that the boiling-point of an alcoholic liquid is lower than that of water in proportion to its alcohol content, and it has been proved by the above investigators that the solids present in beers and wines exert no practical influence on the boiling-point as their molecular weights are so great.

In making an experiment distilled water is first placed in the lower part of the vessel (up to the mark inside), the lid screwed on, the thermometer (graduated in figures showing directly the alcohol-content in volume per cent) inserted in place, the condenser filled with cold water and screwed into the corresponding opening in the lid, and the water heated to boiling by means of the spirit-lamp, which should be shaded by cardboard to prevent draughts. When the water has boiled steadily for a short time the mercury thread of the thermometer (which will have moved gradually along the tube) remains at one point, and the scale of the thermometer is moved by means of the controlling screw until the zero point is coincident with the position of the end of the mercury thread. The water may be boiled until steam begins to escape through the condenser, by which time the zero point will have been accurately ascertained. This determination is required on each day that the instrument is to be used, as this renders any other correction for barometric pressure unnecessary.

After having fixed the zero point the estimation of alcohol in beer may be made. The beer (at any temperature) is filled up to the mark and boiled as described in the case of water. It has been found convenient to take readings at intervals of fifteen seconds, beginning when the regular boiling commences. The true boiling-point is not reached until the beer has been boiling steadily (easily recognised by placing the ear near the top of the condenser, when a continuous bubbling is heard) for some time, when the mercury remains stationary. By this time the condenser will have become hot, and if the boiling be continued the mercury advances again and vapour escapes from the top of the condenser. The following readings, taken at fifteen seconds interval, are quoted in order to show the course of the experiment.

6·4	5·8	True boiling-point.
6·1	5·8	
6·05	5·8	
6·05	5·8	
5·95	5·7	
5·9	5·6	
5·85	5·65	
	5·6	Alcohol escaping.

A determination by the distillation method gave 5·8 per cent. In order to prove the accuracy of the method in the case of English beers, estimations were made of the alcohol-content of a number of various samples purchased at random. The alcohol was determined first by the ebullioscope and secondly by the distillation method. It will be seen that the agreement is quite satisfactory. The alcohol-content is given in volume per cent (cc. of absolute alcohol per 100 cc. of beer; the weight percentage could of course be obtained by a determination of the specific gravity of the beer and a simple calculation).

	Ebullioscope.	Distillation.
Bottled Beers.		
Mann, Crossman, and Paulin's "family ale"	4·75	4·65
Mann, Crossman, and Paulin's "brown ale"	5·0	5·0
Mann, Crossman, and Paulin's "dinner ale"	5·0	4·9
Whitbread and Co.'s "family ale"	5·8	6·0
Whitbread and Co.'s "dinner ale"	5·65	5·75
Meux's "light pale ale"	5·3	5·2
Benskin's "bitter pale"	5·05	4·95
Truman, Hanbury, Buxton, and Co., Ltd., "family ale"	3·75	3·85
Bass's "East India pale ale"	6·3	6·3
Worthington's "India pale ale"	6·9	7·1
Ind, Coope, and Co.'s "Romford ale"	5·5	5·3
Allsopp's "light dinner ale"	5·9 / 5·8	5·85
Allsopp's "India pale ale"	6·25	6·15
Marston, Thomson, and Evershed's, Ltd., "pale ale"	6·3	6·35
Reid's "family stout"	5·3	5·0
Draught Beers.		
Whitbread's "KK Burton pale"	8·8	8·8
Benskin's "India pale ale"	6·2	6·2
Whitbread's "light bitter ale"	5·8	5·8
Whitbread's "mild ale"	6·05	6·15
Lager Beers.		
Allsopp's "Lager"	4·6	4·5
Imported German "Pilsener"	4·7	4·8
Imported German "Munich"	4·3	4·2

My thanks are due to Sir William Ramsay, K.C.B., for suggesting this work, and for affording me facilities for carrying it out at University College.

AN ACCURATE METHOD OF ANALYSIS OF ALUMINIUM.

By HARI PADA BHATTACHARYYA, M.A.

Total Silicon.—Weigh 1 grm. in a porcelain basin, and add to it 20 cc. strong HNO_3 (sp. gr. 1·45), and keep it covered on the hottest part of a hot plate. The metal will dissolve with evolution of nitrous fumes. The cover is then removed, and the solution is allowed to evaporate down to dryness. The basin is taken away from heat and allowed to cool. When cool, 15 cc. of HCl is added and the solution is evaporated down and baked, and again dissolved in 15 cc. HCl. When the solution becomes clear, 15 cc. of water is added. This is now boiled and taken away to cool, and then filtered through Swedish filter-paper and washed with warm hydrochloric acid and cold water, and afterwards with hot water till the last trace of acid is removed. The residue is ignited wet in a silica crucible and weighed. It is then treated with HF and H_2SO_4 in the usual way.

(N.B.—15 cc. HCl and 5 cc. H_2SO_4 were also tried; the result was not different).

Iron.—Dissolve in a beaker 1 grm. of drillings in 30 cc. of a 25 per cent solution of chemically pure NaOH. As soon as the solution is clear filter it and wash with hot water till the last trace of alkali is removed. Dissolve the residue in warm HCl (1 : 1), and wash the filter-paper with hot water.

Precipitate Fe with ammonia and estimate gravimetrically. (When there is much copper it requires to be dissolved in dilute HNO_3 warm and added to the HCl solution, then precipitate Fe with HN_4HO; Cu will show blue filtrate).

Copper.—Pass SH_2 through the filtrate from SiO_2, and estimate Cu as CuO.

Aluminium.—The filtrate, after the removal of the copper sulphide as above, is boiled to remove SH_2, and then diluted to make up 1 litre, 100 cc. of which is taken for estimation of aluminium. Add 1 grm. Na_3PO_4; dilute to about 200 cc.; neutralise with ammonia to precipitation, and just re-dissolve with a drop or two of HCl. Boil and add sodium thiosulphate solution in excess. (N.B.—If thiosulphate is added to the cold solution it bumps violently when boiling). Boil till the smell of SO_2 is no longer perceived, and then allow to settle. Filter and wash with boiling water till the washings are free from alkaline phosphate (to be tested with $AgNO_3$ solution). The precipitate filters and washes quickly. Ignite in a silica crucible, and weigh as $AlPO_4$. (Factor 22·22 per cent Al). The following are the reactions that take place:—

I. $Al_2Cl_6 + 2Na_3PO_4 = Al_2P_2O_8 + 6NaCl$.
II. $Al_2P_2O_8 + 6HCl = Al_2Cl_6 + 2H_3PO_4$.
III. $2H_3PO_4 + 3Na_2S_2O_3 = 2Na_3PO_4 + 3(S + SO_2 + H_2O)$.

Or expressed in one—

IV. $Al_2Cl_6 + 2Na_3PO_4 + Na_2S_2O_3 + 2HCl = Al_2P_2O_8 + 8NaCl + S + SO_2 + H_2O$.

Zinc.—The filtrate from the precipitation of Al is made ammoniacal and boiled till the solution shows amphoteric reaction to litmus-paper. Filter and wash with boiling water. Ignite and weigh as $Zn_2P_2O_7$ (Zn = 42·91 per cent). The following reactions take place:—

I. $Na_2S_2O_3 + 2HCl = 2NaCl + H_2O + S + SO_2$.
II. $Zn_3(PO_4)_2 + 6HCl = 3ZnCl_2 + 2H_3PO_4$.
III. $H_3PO_4 + 3NH_4HO = (NH_4)_3PO_4 + 3H_2O$.
IV. $ZnCl_2 + (NH_4)_3PO_4 = NH_4ZnPO_4 + 2NH_4Cl$.
V. $2(NH_4)ZnPO_4 = Zn_2P_2O_7 + H_2O + 2NH_3$.

Sodium.—This is estimated by the usual method, viz., solution in strong nitric acid (1·45 sp. gr.) is evaporated to dryness and baked; 5 cc. HNO_3 is added again, and again dried and baked, then ignited to drive off nitrous fumes, cooled, and crushed to powder; added boiling water, boiled, the clear liquid decanted, and the residue washed with boiling water. The whole is evaporated down to dryness. Dissolve the residue in 25 cc. hot water, and add a drop of NH_4HO to see if there is any Al present. Convert to chloride and weigh, &c.

The following experiments may prove of interest:—

1. 0·1 grm. aluminium (99 per cent purity) and 0·1 grm. Zn (99·95 per cent purity) were weighed in a beaker and dissolved in HCl, and aluminium was separated, washed, dried, and ignited; from the filtrate Zn was estimated as pyrophosphate. The following figures were obtained:—Al = 0·099 grm.; Zn = 0·09995 grm.

2. 0·1 grm. aluminium (99 per cent purity) was weighed in a beaker and dissolved in HCl, and Al was estimated by the method. 0·099 grm. was the figure obtained. The filtrate was free from aluminium.

3. 0·1 grm. zinc was weighed in a beaker and dissolved in HCl. The excess acid was boiled out, diluted, added sodium phosphate, the precipitate cleared with HCl, boiled, and added hypo solution, boiled, filtered, and washed. The filter-paper is ignited and weighed.

Ash.—0·00056 obtained, which was the ash of 11 cm. Swedish filter-paper, showing that Al precipitate is not contaminated with Zn.

The filtrate is treated for Zn. Zn weighed 0·09995 grm.

The above experiments show the accuracy of the method.

Carbon.—This has been determined by the sodio-copper chloride process. But this reagent must be added gradually drop by drop over water (25 cc.) in which the aluminium drillings are placed, otherwise a too violent action will take place and some C will be lost. Filter the carbon through asbestos, and estimate it by a wet combustion as usual.

Gun and Shell Factory, Ishapore, Bengal.

PASSIVITY.*

By GERHARD C. SCHMIDT.

1. *Introduction.*

Although the abnormal chemical and electrochemical behaviour of iron and certain other metals has been known for more than 100 years, up to the present no explanation of the cause of passivity has met with general acceptance. In course of time many theories have been suggested and subsequently given up. At the present time only two theories deserve serious consideration: (a) the oxide theory of Faraday, according to which passivity is due to a coating of oxide or oxygen on the metal—a theory which still finds supporters in spite of the many serious objections put forward against it—and the hydrogen theory, according to which the metals in question are normally passive and become active only in the presence of dissolved hydrogen acting as a catalyst. The latter view has recently been strongly supported by my pupils, Grave (*Zeit. Phys. Chem.*, 1911, lxxvii., 513) and Adler (*Ibid.*, 1912, lxxx., 385), on the basis of experimental investigations. Flade ("Habilitationsschrift," Marburg, 1910; *Zeit. Elektrochem.*, 1912, xvii., 335) does not regard their results as conclusive, and considers that his own investigations lend support to the oxide theory. In the present Paper the results of further experiments designed to decide between these two theories are described.

2. *Criticism of Flade's Results.*

Flade found that iron rendered passive by anodic polarisation in dilute sulphuric acid immediately returns to the active state when the polarising e.m.f. is removed.

When, however, it is in a circuit and forms the anode under the influence of an external, not too great, e.m.f., the potential gradually becomes more negative, until at a certain potential, the "transition point," it suddenly

* A Contribution to the General Discussion on "The Passivity of Metals" held before the Faraday Society, November 12, 1913. (Experimental Part by W. Rathert.)

becomes active. Flade regards this point as the long sought limit between the active and passive states.

The arrangement used by Flade is practically identical with that of Fredenhagen (*Zeit. Phys. Chem.*, 1908, lxiii., 1), and the question arises whether the transition point discovered by Flade is not the "activation potential" of Fredenhagen. If this should prove to be the case it follows, since Fredenhagen has shown that the "activation potential" and the "passivation potential" are quite different, that the formation of well-defined oxides is excluded. This point was first investigated.

3. *Experimental Results.*

As a result of investigations which will be fully described elsewhere, it was found that the "transition point" is in fact identical with the activation potential of Fredenhagen, and, further, that in all cases the activation potential and the passivation potential are different. The transition point does not form a boundary between the active and the passive states, since iron can remain active at a potential which is much more positive (more noble) and passive at a potential much more negative than that corresponding with the transition point. Further, experiments with wires of different lengths show that the transition point has not always the same value. In fact, the determining factor in these investigations is the current density, or in other words the amount of oxygen set free by the current. The investigations of Flade furnish evidence against the oxide theory, since, as Fredenhagen has pointed out, the activation and passivation potentials must coincide if oxides are formed. On the other hand, the results in question can readily be accounted for on the basis of the hydrogen theory. When iron is rendered passive by anodic polarisation, the oxygen combines with the hydrogen diffusing through the iron towards the surface and thus retards solution of the metal. The iron remains passive as long as the oxygen is being liberated freely. As the amount of oxygen liberated falls off with diminishing current density a point is reached when it is no longer sufficient to combine with all the hydrogen. The iron becomes active at one point; hydrogen is immediately set free at this point, neighbouring regions become active as a consequence of local currents, and thus the whole surface becomes active with explosive rapidity. When the attempt is now made to reverse the condition of the metal, considerable resistance is met with on account of the considerable content of hydrogen and its high absorptive power for this gas. As the rate of liberation of oxygen increases, the potential gradually becomes more positive (nobler), the metal becoming passive at certain points: at other points solution of the metal proceeds and the evolved hydrogen tends to remove the passivity. As the current density and the consequent liberation of oxygen are further increased, more and more of the metal is rendered passive, until a point is ultimately reached at which the tendency to activity is overcome and the whole of the metal becomes passive. This change cannot proceed with the same rapidity as the converse one, on account of the strongly marked tendency of iron to remain active, and it is therefore not to be anticipated that the activation and passivation potential will coincide—a conclusion fully confirmed by experiment.

The behaviour of chromium is the converse of that of iron, the active condition in this case being the normal. Corresponding with this the transition point with evolution of hydrogen is quite sharp.

4. *The Effect of Polishing.*

Although the results of Flade and those subsequently obtained in the Münster laboratory can be explained on the hydrogen theory, they do not constitute a conclusive proof of the validity of that theory. The results described below allow, in my opinion, of a definite decision between the two theories.

The guiding principle in these investigations is as follows: According to Muthmann and Frauenberger (*Sitzungsber. Kgl. Bayr. Akad.*, 1904, xxiv., 201) passivity is brought about by the presence of oxygen dissolved in the metal. Flade accepts this view only as regards the action of air in causing passivity; all other passivity phenomena are ascribed to the formation of oxide films on the metal. On either of these assumptions any metal the surface of which is cleaned in the entire absence of oxygen must be active, whilst according to the hydrogen theory it is to be anticipated that iron, which always contains hydrogen, would be active, and chromium and nickel, which do not contain hydrogen, would become passive.

In order to test these conclusions an apparatus was constructed in which the metals could be subjected to friction in an atmosphere of hydrogen or nitrogen and the potentials then determined at once. The gases were very carefully purified and air was completely excluded. It was found that when subjected to friction in hydrogen, chromium and nickel became rather more positive (nobler) but remained completely passive. These results show conclusively that metals may remain passive in the absence of oxygen, under circumstances in which the formation of an oxide film is impossible—results which cannot be reconciled with the oxide theory. The small differences of potential observed when metals are subjected to friction in different gases are due to adhering layers of gas. Iron, on the other hand, was always found to be active even in neutral solutions of ferrous sulphate: it is naturally a less noble metal than chromium or nickel, and, as the investigations of Belloc (*Ann. Chim. Phys.*, 1909, xviii.) and others have shown, always contains considerable amounts of hydrogen.

5. *Effect of a Hydrogen Charge on the Potential and Activity of a Metal.*

In the foregoing sections it has been proved that metals which contain no alloy with oxygen and are free from coatings of oxide can retain the passive condition, but in order to show the validity of the hydrogen theory it is further necessary to prove that dissolved hydrogen can transform metals from the passive to the active form. For this purpose metals prepared by electrolytic methods and therefore containing hydrogen were examined; and, further, hydrogen was liberated at a point and conveyed by diffusion to other passive portions of the surface, under which circumstances the passive portions regained their activity.

As already mentioned, ordinary iron is active in ferrous sulphate solution, probably owing to the large proportion of hydrogen it contains. Electrolytic iron is also active under these conditions, showing a less noble potential than ordinary iron. The potential $\epsilon_h = -0.66$ volt found by Muthmann and Frauenberger (*loc. cit.*), is, as shown by Richards and Behr, too high; it represents the potential o iron supersaturated with hydrogen. The value $\epsilon_h = -0.423$f volt obtained by us in good agreement with that given by2 Richards and Behr, is also that of a metal containing hydrogen. Muthmann and Frauenberger found that the potential can be made more negative (less noble) by adding more hydrogen, and it seems plausible to assume that by the withdrawal of hydrogen the potential will become more positive, and that finally the metal will become passive. These conclusions cannot be satisfactorily tested experimentally, as the amount of hydrogen in iron in any given case is not known and the gas cannot be completely removed from the metal.

The matter can, however, br tested in the case of nickel and of chromium. Ordinary nickel in nickel sulphate and chromium in dilute sulphuric acid are completely passive. On the other hand, electrolytic nickel and chromium, which are both highly charged with hydrogen, are active and go into solution with evolution of hydrogen. (According to Carveth and Curry, *Journ. Phys. Chem.*, 1905, ix., 353, electrolytic chromium contains 250 times its volume of hydrogen). If chromium is deposited

electrolytically on a sample of the same metal prepared by the Goldschmidt process, and which is quite inactive, the latter under the influence of the hydrogen also dissolves in dilute sulphuric acid. His results are in entire agreement with those of Hittorf, who showed that even the minute trace of hydrogen liberated at a chromium electrode by making it a cathode for a moment renders the metal active. In my investigations just described the hydrogen which starts the reaction is contained in the electrolytic iron. The phenomena just described, at least as far as chromium and nickel are concerned, must be regarded as "experimenta crucis" in favour of the hydrogen theory. When the metals are prepared electrolytically or by reduction at a high temperature and subsequent rubbing in an atmosphere of hydrogen, they differ only in electrochemical behaviour and in the extent to which they are charged with hydrogen. The assumption that these two factors are in casual connection cannot be avoided, especially as the possibility of the formation of oxides or alloys with oxygen is excluded.

The experiments with iron are, however, not decisive, since it always remained active. The following investigations supply the evidence required.

(To be continued).

THE

MANUFACTURE OF HYDROGEN FOR BALLOONS.

PORTABLE PLANTS FOR MILITARY USE.

THE progress recently made in developing balloons and airships for military and other uses has caused increased attention to be paid to methods for producing hydrogen gas in large quantities and in a sufficiently pure state. Of late the extensive use of airships in some countries as a part of the army outfit has led to a search for suitable hydrogen-producing plants especially adapted for military use. Fixed hydrogen plants are of course useful in connection with aeronautic establishments and army centres, but what is especially valuable now is a portable outfit; by the adoption of a hydrogen plant mounted upon railroad cars it will be seen that the effective work of an airship will be at once increased. Similarly the gas from such a movable plant can be used in different industries developed within the last few years, such as electric welding of plates or bars, and similar work, for which a considerable amount of hydrogen is needed at present, also for cutting plate iron by the hydrogen blowpipe.

The hydrogen-producing methods used mainly up to now are purely chemical, electrolytic, or regeneration processes, but all have their disadvantages as compared with the oil-gas method. In some cases the first cost or operative expenses are high, and in others the gas needs to be produced on the spot where hydraulic or other cheap electric power can be employed, or in other cases where a water-gas plant can be installed to advantage. Some processes do not give a pure enough hydrogen; for example, the gas for use in airships must be free from chlorine, for chlorine attacks the balloon envelope.

According to the new German hydrogen process devised by Rincker and Wolter, the gas can be produced in any suitable place, and the plant occupies but a small space, with a very cheap production. At the same time the compact shape of the apparatus makes it very well adapted for mounting upon cars so as to give a portable plant for airships. The gas which is produced in this apparatus has only a small percentage of nitrogen and has a specific gravity of 0·087 to 0·092. The operation is based upon the use of crude oil to produce the gas, or the producer can be made to work on benzene, refined oil, benzoyl, and the like. Heating is done by the use of coke as a general rule, although this can be replaced by charcoal. The plant is mounted upon two railroad cars, the first of which carries the gas producer layout, while the second has the remainder of the plant, including the cooler, scrubber, and other purifying devices.

The main apparatus on the front car consists of a pair of gas producers. Each of these has a heavy plate iron casing, which is lined with fire-brick. To remove slag and ash there are two doors in the front which are kept closed while the gas is being produced. On the top of the apparatus is a hopper for use in feeding in the coke. At the bottom of the producer are good-sized pipes which bring in the air-blast from the blowing chamber. The first of the two producers also has an oil spray for introducing the oil at the top part. The producer is filled up with coke, and hot air is sent in at the bottom, coming from a steam turbine driven blast-fan, this being worked by the steam from the locomotive. If need be, the blast-fan can also be driven by a gasoline motor or crude oil engine of the usual kind in the case of the portable plant, or with a stationary plant a gas engine, electric motor, or any suitable mechanical drive can be used.

Oil for the spray is supplied by a suitable oil pump, which feeds from a large tank on the car. It is necessary to heat this oil before feeding it into the producer, and the steam from the turbine is brought to the tank for this purpose, so that the heating is economically done. At the start of the apparatus both producers are filled with coke and fired up. By the use of the hot-air blast the coke is brought to a white heat, and during this time the coke gases are carried off through the opened top cover and escape into the air through the plate iron chimney. The blast is now stopped and the top cover closed down, whereupon the oil spray is set working, and the oil is transformed into oil-gas, this being obliged to pass through the heated coke of the two generators in succession. In this way all the light as well as heavy hydrocarbons are decomposed, and the result is a high grade of hydrogen gas containing from 90 to 96 per cent pure hydrogen. Before the producer is actually working to deliver the pure gas to the rest of the apparatus, care is taken to evacuate the gas which was already contained in the producers, and the first part of the newly produced hydrogen is allowed to escape by a special valve which is fitted on for this purpose, according to a patented method. During the usual working of the producers the passage of the gases through the hot mass of coke causes the temperature of the coke to become eventually lowered, and when it cools down below a certain point no more gas will be generated. When this is the case the oil feed is stopped, and the hot-air blast again turned on so as to fire up the coke mass as was done in the first place. Then the oil spray is turned on and the process repeated. Thus the method is an intermittent one, and consists in an alternate operation of the oil spray and hot blast. Firing up the coke by the blast usually takes two or three minutes during the run, that is, when the coke is still hot, then the gas production lasts for about twenty minutes, and so on.

From the second producer the gas goes by good sized piping into a device which is provided with a water seal in order to prevent a back flow of gas during the period when the hot-air blast goes through the producer. Care is taken in all cases to keep the hydrogen from becoming mixed with air. The gas then passes into the second car by means of coupled piping. On the front end of the car is mounted a well designed scrubber, which is designed with water flow so as to clear the gas of all mechanical impurities such as ash or soot. The scrubber consists of a plate iron case, which is filled up with the washing elements of patented make up, a water flow being introduced at the top, while the gas comes in at the bottom of the scrubber. Means are provided for effectively dividing up the gas flow in small streams so that it comes into as good contact as possible with the water.

Next the gas comes into a cleaner which works on a dry process, and is designed to remove any sulphur compounds contained in the gas. The gas is now sufficiently pure for many industrial purposes, as may be seen from the following analysis:—

	Per cent.
CO_2	0·0
O	0·0
CO	2·7
CH_4	0·0
H	96·0
N	1·3

The specific gravity of the gas is about 0·10. Next, the gas is freed from moisture by sending it through a sulphuric acid dryer, and lastly it passes through a heating furnace for removing the carbon monoxide, the furnace being heated by oil-gas. Then the gas goes to a cooler, which is built together with the first-mentioned scrubber. Analysis is then as follows:—

	Per cent.
CO_2,O,CH_4	0·0
CO	0·4
H	98·4
N	1·2

Specific gravity = 0·087 to 0·092.

Firing up takes one to two hours, and the plant can run for months at a time, needing but two men. The plant follows the airship, and either supplies it direct or, where too far off, by a special outfit provided with steel gas bottles. To this end a third car can contain a compressor plant for charging the bottles.—Abridged from the *Scientific American*, cix., No. 24.

THE SCIENTIFIC WEEK.

(*From Our Own Paris Correspondent*).

THE REJUVENESCENCE OF THE POTATO.

The potato is a plant grown old and weakened by four hundred years of unsexed reproduction; it is the same plant that has been propagated for several centuries by the multiplication of its tubercles by slips or cuttings. How can the potato be rejuvenated? M. Sartory, Doctor of Science, of Nancy, and MM. Gralift and Thiebaut have examined this problem. In the name of these three scholars, M. Guignard, Professor of the Higher School of Pharmacy, has presented to the Academy of Sciences a paper, in which they show that edible tubercles can be obtained from the cultivated seed of the potato. However, this can only be arrived at by the help of certain fungi of the soil, which fix on to the plant and provoke the formation of the tubercles. In the spring of 1912, M. Sartory and his collaborators obtained from sowings, sixty plants which all bore tubercles in a greater or less number, the average size of which was about that of a walnut. Some of these potatoes weighed as much as 150 grms. Those that were in a good condition were able to be preserved and planted in 1913. They all produced vigorous plants free from disease. The new race is quite free from all imperfection, whereas the neighbouring potatoes were more or less attacked by various diseases. The putting into practice of this method of culture of potatoes by sowing will allow of the rapid regeneration of this precious tubercle; at the same time by crossings and selections it will be possible to obtain varieties presenting qualities desirable from an alimentary as well as from an industrial point of view. This discovery may have very important economical consequences.

THE BIRTH OF TUBERCLES.

To complete the paper presented by M. Guignard, Dr. Roux, Director of the Pasteur Institute, has informed the Academy of an interesting study by M. Magron, which shows that tuberisation takes place in the sown potato, thanks to a microscopic fungus belonging to the family of mucors, and which is moreover the parasite of the bitter-sweet. The tubercles are born only if these fungi penetrate into the prolongations of the subterranean roots of the potato. The tuberisation is then thus caused by parasitism. The same facts are to be observed in orchids that can only be propagated by symbiosis. Fresh researches still kept secret will shortly revolutionise the culture of these precious and rare flowers.

BITTERNESS OF BURGUNDY WINES.

Certain of the finer quality wines of Burgundy have from time to time an inexplicable bitter taste, which is very disagreeable to connoisseurs and lovers of good wine. The origin of this bitterness had always remained unknown. A Professor of the Faculty of Science of Dijon has just made a most curious discovery concerning this fact. In a communication presented to the Academy by Prof. Armand Gautier, M. Voisinet shows that in drinkable waters there exists a microbe that possesses the property of dehydrating glycerin and giving acrolein, which becoming resinous produces the bitter that is so dangerous for the fine Burgundy wines. If this new ferment of M. Voisinet is, as he proves it to be, identical with that of the bitterness of these fine wines, it is easy to understand that it suffices to wash the bottles with spring water to introduce into those bottles the ferment that modifies so unfortunately, although only temporarily, the taste of these superior quality Burgundies.

A NEW INDICATOR OF FIRE-DAMP.

Fire-damp or coal-dust produce terrible catastrophies in mines. This carburetted hydrogen is inoffensive as long as it is only present in the mine in small quantities; but when the amount contained in the atmosphere exceeds the explosive limit, that is to say, 5·5 per cent, the miner's life is in danger if this explosive mixture should take fire. Safety lamps, those lamps of gauze wire invented by the English chemist Davy, have prevented many accidents. These lamps, which to-day are but little used on account of the weak light they give, may be employed as indicators of possible explosions. A practised eye, when the wick is lowered and when surrounded by a fire-damp atmosphere, can perceive a luminous halo, which becomes notably clearer and stronger as the explosive limit approaches. When large quantities of unbreatheable gas arrive the lamp goes out. And yet many have tried to discover indicators or warners of carburetted hydrogen freed from all possibility of accidental inflammation. Two *savants*, Prof. Haber and Dr. Leiser, have just discovered an indicator which no longer addresses itself to the eye but to the ear, which organ acquires a great acuteness in the silence of the mine. They have imagined a whistle for fire-damp mines. It is a wire cylinder 25 cm. long and 5 cm. in diameter, formed by two whistles with closed lips, which are in unison, for one gas, and which are worked and put in movement by the same current. One of these whistles is filled with pure air. The tube of the other whistle is filled with the air of the mine. When the apparatus is made to act, if the air of the mine is pure only one sound is heard. If the gas of the whistle contains 1 per cent of methane, it is easy to hear two beats per second. When the quantity of methane increases, the beats augment rapidly, and in the neighbourhood of the explosive limit this phenomenon is transformed into a veritable trill. These differences of sound are easily perceived, and in the galleries of the mine they are still quite clear at a distance of 100 metres.

Catalytic Etherification in Aqueous Solution of Primary Alcohols of the Series $C_nH_{2n+2}O$.—F. Bodroux.—Formic, acetic, and propionic acids can be etherified by primary alcohols of the series $C_nH_{2n+2}O$ by distilling, in presence of a small quantity of catalyst, a mixture of the acid and alcohol diluted with a large quantity of water. The author has obtained a good yield of ethyl phenylacetate by mixing equal weights of phenylacetic acid, ethyl alcohol, and hydrochloric acid.—*Comptes Rendus*, clvii., No. 20.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, December 4th, 1913.

Prof. W. H. Perkin, LL.D., F.R.S., President, in the Chair.

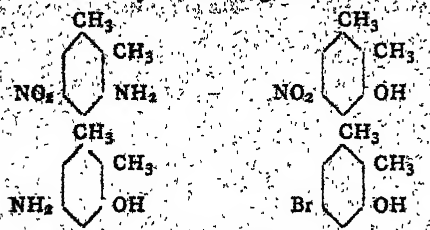
(Concluded from p. 35).

313. "*The Optical Rotatory Power of Derivatives of Succinic Acid in Aqueous Solutions of Inorganic Salts.*" Part I. By George William Clough.

The specific rotations of *d*-tartaric acid, methyl *d*-tartrate, ethyl *d*-tartrate, and *d*-tartramide respectively have been measured at various temperatures in aqueous solutions of sodium and barium haloids. The values obtained are in all cases lower than those for the corresponding aqueous solutions. The results were discussed from the point of view of Armstrong and Walker's hypothesis (*Proc. Roy. Soc.*, A, lxxviii., 388).

314. "*Derivatives of* o-*xylene.* Part VI. 5-*Bromo*-o-3-*xylenol.*" By Arthur William Crossley.

5-*Bromo*-o-3-*xylenol* has been synthesised by a series of reactions indicated by the following formulæ :—



It crystallises from light petroleum (b. p. 40—60°) in radiating clusters of glistening needles, melting at 84°, and is identical with the bromoxylenol, of similar melting point, obtained by the action of phosphorus pentabromide on dimethyldihydroresorcin (*Trans.*, 1903, lxxxiii., 128).

The *benzoyl* derivative crystallises in rhombic plates, melting at 98°, and the o-*nitrobenzoyl* derivative separates from alcohol in transparent needles, melting at 128°.

315. "*The Condensation of Chloral Hydrate and Carbamide.*" By Noel Guilbert Stevenson Coppin and Arthur Walsh Titherley.

The two derivatives obtained by Jacobson (*Annalen*, 1871, clvii., 246) in the condensation between chloral hydrate and carbamide are *β-trichloro-α-hydroxyethylcarbamide*, $CCl_3 \cdot CH(OH) \cdot NH \cdot CO \cdot NH_2$ (I.), and *di(β-trichloro-α-hydroxyethyl)carbamide*,

$$CCl_3 \cdot CH(OH) \cdot NH \cdot CO \cdot NH \cdot CH(OH) \cdot CCl_3 \quad \text{(II.)}.$$

They are formed by a reversible change whenever the reactants are present in equimolecular proportion in aqueous solution; with concentrated solutions the compound (I.) greatly predominates unless a mineral acid catalyst is present, which favours the production of (II.). When one molecular proportion of chloral hydrate acts on two of carbamide, however, the formation of the compound (II.) is prevented, unless a mineral acid is present. Both substances are slowly hydrolysed into chloral hydrate and carbamide on heating with water. Thus, in 50 per cent aqueous solution at 70, β-trichloro-α-hydroxyethylcarbamide suffers decomposition to the extent of about 50 per cent in an hour. The mixture which separates on cooling contains about 70 per cent of compound (I.) and 30 per cent of compound (II.) :—

In the reversible system :—

$$\text{Water} + \beta\text{-trichloro-}\alpha\text{-hydroxyethylcarbamide} \rightleftharpoons \text{chloral hydrate} + \text{carbamide},$$

the true equilibrium is virtually never reached, owing to continual formation of di(β-trichloro-α-hydroxyethyl)-carbamide, which, being nearly insoluble, separates out.

β-Trichloroethylidenecarbamide, $CCl_3 \cdot CH{:}N \cdot CO \cdot NH_2$ (m. p. 234°), is readily obtained from β-trichloro-α-hydroxyethylcarbamide by the action of acetic anhydride on its solution in alkali.

Trichloroethylidenedicarbamide, previously obtained by Pinner and Lifschütz (*Ber.*, 1887, xx., 2346) from chloralcyanohydrin and carbamide, is produced slowly when β-trichloro-α-hydroxyethylcarbamide is heated at 100° with carbamide and acetic anhydride.

316. "*The Action of Amino-acid Esters on Ethyl Dicarboxyglutaconate.*" By Stanley Isaac Levy.

The reaction between ethyl dicarboxyglutaconate and organic derivatives of ammonia, which has been investigated by Ruhemann and his pupils, has now been extended to α-amino-acid esters. It has been found to apply generally to compounds of this class, and derivatives have been prepared from the esters of glycine, alanine, aminobutyric and amino*iso*butyric acids, and leucine. With the exception of the first member of the series, *ethyl glycylmethylenemalonate*, $CO_2Et \cdot CH_2 \cdot NH \cdot CH{:}C(CO_2Et)_2$, which is a colourless solid, these compounds are yellow, viscous oils; in chemical behaviour they closely resemble ethyl aminomethylenemalonate. Thus they are easily decomposed by acids or alkalis, and are not reduced by the zinc-copper couple; when heated with aniline, they yield the monoanilide of ethyl anilinomethylenemalonate.

317. "*The Relationship between tha Absorption Spectra and the Constitution of Ketones and their Derivatives*" (Part I.). By George Gerald Henderson, James Alexander Russell Henderson, and Isidor Morris Heilbron.

The authors have re-examined the absorption spectra of a series of carefully purified aliphatic ketones, and have found that the characteristic absorption band of acetone is shown by all these compounds, and that the persistence of the band is in each case fully equal to that of the acetone band.

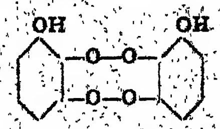
In order to account for these and other facts the authors suggest that the selective absorption of ketones is due to intramolecular vibrations caused by the momentary formation of unstable ring systems through the agency of free "partial valencies," which, under certain conditions, make their appearance on the atoms of the carbonyl group.

318. "*Note on Purpurogallin.*" By Arthur George Perkin.

In view of the fact that the author has been engaged for a long time with the study of purpurogallin (Perkin and Steven, *Trans.*, 1903, lxxxiii., 192; 1906, lxxxix., 802; A. G. and F. M. Perkin, *Ibid.*, 1904, lxxxv., 243; 1908, xcvii., 1186; A. G. Perkin, *Proc.*, 1905, xxi., 211; *Trans.*, 1912, ci., 803; 1913, ciii., 661), the recent paper of Nierenstein and Spiers (*Ber.*, 1913, xlvi., 3151) requires comment. These authors, who have repeated the earlier work of Perkin and Steven (*loc. cit.*), already partly confirmed by Herzig (*Monatsh.*, 1910, xxxi., 799), with identical result, claim to have established the presence of four hydroxyls in this compound, notwithstanding the fact that, tetra-acetylpurpurogallin, monoacetylpurpurogallin trimethyl ether (*loc. cit.*, 1903), and purpurogallin tetramethyl ether (*loc. cit.*, 1905) have been prepared. Although acetylpurpurogallin was described as yellow by Nietzki and Steinmann (*Ber.*, 1887, xx., 1277) and Perkin and Steven (*loc. cit.*), Herzig isolated this compound in the colourless condition, whereas Nierenstein and Spiers can only prepare an orange-yellow product. A colourless substance can, however, easily be obtained by crystallising from benzene with animal charcoal, although in the author's experience this purification is much more difficult to effect with acetic acid or alcohol. It is interesting to note that no distinction in melting-point can be observed between the yellow and colourless preparations, from which it appears possible that the pure acetyl compounds exist in two forms. This purpurogallin, regenerated from the latter variety, on reacetylation with acetic anhydride

and pyridine yields the usual yellow product, which shows the same behaviour with solvents.

Nierenstein and Spiers refer also to the compound $C_6H_4O_3$(?), first prepared by the oxidation of pyrogallol by means of *iso*amyl nitrite (*loc. cit.*, 1906), but more recently by means of *p*-benzoquinone (*loc. cit.*, 1913), which yields purpurogallin among other products when digested with boiling water. By the *p*-benzoquinone method (20 grms. of pyrogallol, 6 grms. of *p*-benzoquinone, and 15 cc. of absolute alcohol), the yield of 0·51 grm., although larger than that given by *iso*amyl nitrite (0·27 grm.), is so small that in the hope of the discovery of a better process which, however, has not been forthcoming, the author until recently hesitated to prepare a quantity of the material by these expensive methods. Although it suggested itself as possible that the production of this compound from pyrogallol was in reality due to the presence of traces of a second compound in this substance, this seems not to be the case, because pyrogallol, when submitted to the action of zinc dust and dilute acid, still reacts in the same way with *p*-benzoquinone. Whereas the constitution at first preferred for the compound $C_6H_4O_3$(?) was that of a hydroxy-*o*-benzoquinone, Willstätter and Müller (*Ber.*, 1911, xliv., 2180) consider this to be unlikely, and further work now in progress favours the second or peroxide formula, already alluded to in the earlier communication.



Nierenstein and Spiers have again examined the product of the distillation of purpurogallin with zinc dust, although Nietzki and Steinmann and also Perkin and Steven obtained napthalene thereby, and it has been very recently shown that by the reduction of purpurogallone both β-naphthol and 2 : 3-dihydroxynaphthalene can be produced. If purpurogallin, as now seems probable, is in reality a naphthalene derivative, the simple expression $C_{10}H_4(OH)_4CO$ is only available for it. In such a case it has suggested itself to the author among other considerations that the *o*-quinonoid grouping, $\begin{matrix} \diagdown \\ C{:}CH{\cdot}OH \\ | \\ C{:}O \\ \diagup \end{matrix}$ is present, because the isomeric purpurogallone derived from it by the action of alkali at a high temperature, which has the properties of a trihydroxynaphthalenecarboxylic acid, can thus be regarded as a product of simultaneous oxidation and reduction. Such a grouping would also account for the comparative resistance of the fourth hydroxyl in purpurogallin to methylation, and again, the formation of the colourless acetyl and tetramethyl derivatives could be explained on the assumption that these exist in the tautomeric hydroxy aldehydic condition. A formula involving the grouping $\begin{matrix} \diagdown \\ C{:}CH_2 \\ | \\ C{:}O \\ \diagup \end{matrix}$ also suggests itself, and these points are mentioned here in that the work on which the author is now engaged, and which consists mainly of a study of the oxidation of the purpurogallin methyl ethers, involving as it does the preparation of large quantities of material, will occupy a considerable time.

319. "l-*Epicamphor* (l-β-*camphor*)." By Julius Bredt and William Henry Perkin, jun.

A detailed description of work of which a preliminary account has already appeared (*Proc.*, 1912, xxviii., 56).

320. "*The Action of Hydrogen Peroxide on the Sodium Alkyl Thiosulphates.*" By Douglas Frank Twiss.

Dibenzyl diselenide has been submitted to oxidation (both electrolytic and by hydrogen peroxide) in the hope of producing compounds of the selenoxide, selenone, or selenonium salt class (compare Fichter and Sjöstedt, *Ber.*, 1910, xliii., 3422), but the result of such treatment was to eliminate the selenium from the molecule either in the free state or as selenious acid.

In consequence of the lack of success attendant on experiments in this direction, the effect of oxidation of sodium or potassium alkyl selenosulphates was considered as a possible process for the achievement of the desired end. The action of hydrogen peroxide was therefore first tried with sodium alkyl thiosulphates, when it was found that in acid solution this process gives rise to excellent yields of the corresponding disulphides even at the ordinary temperature. Dibenzyl, di-*o*-nitrobenzyl, di-*p*-nitrobenzyl, and diallyl disulphides were prepared in this manner. Under similar treatment, potassium *o*-nitrobenzyl selenosulphate produced di-*o*-nitrobenzyl diselenide.

321. "*Synthesis of* d- *and* l-*Sylvestrene.*" By Walter Norman Howarth and William Henry Perkin, jun.

A detailed description of work of which a preliminary account has appeared (*Proc.*, 1910, xxvi., 97; 1913, xxix., 223).

322. "*Note on the Configurations of the Optically Active Normal Secondary Alcohols.*" By George William Clough.

Pickard and Kenyon have prepared ten optically active carbinols of the series $CH_3{\cdot}CH(OH){\cdot}R$ (the "methyl" series), eight of the series $CH(CH_3)_2{\cdot}CH(OH){\cdot}R$ (the "*iso*propyl" series), and thirteen of the series $C_2H_5{\cdot}CH(OH){\cdot}R$ (the "ethyl" series). The simplest carbinol of the "methyl" series and of the "ethyl" series is methylethylcarbinol. Pickard and Kenyon have made a comparison of the molecular rotatory powers of the dextrorotatory carbinols of the "methyl" and of the "ethyl" series, and have selected the dextrorotatory form of methylethylcarbinol for comparison with the dextrorotatory carbinols of both series (*Trans.*, 1911, xcix., 45; 1912, ci., 620; 1913, ciii., 1923).

Although it is impossible to state with certainty that the carbinols possessing the same sign of rotation are configuratively similar, it appears highly probable that in the case of the higher members of a series similarity of sign does indicate similarity of configuration. The assumption may therefore be made (and the course of the curves for the molecular rotations strongly supports this view) that in the "methyl" series where $R > CH_3$ (that is, in all cases), and in the "ethyl" series where $R > C_2H_5$, similarity of sign of rotation accompanies similarity of configuration. Moreover, if the two series of carbinols, $CH_3{\cdot}CH(OH){\cdot}R$ and $C_2H_5{\cdot}CH(OH){\cdot}R$, are compared, it appears exceedingly probable from a consideration of the curves representing the molecular rotations in the homogeneous state, in benzene solution and in ethyl alcoholic solution respectively, that the higher dextrorotatory carbinols of the "methyl" series are configuratively similar to the dextrorotatory carbinols of the "ethyl" series. Thus, if $R > C_2H_5$, the corresponding dextrorotatory carbinols of the two series may be configuratively represented by the formulæ—

$$\begin{matrix} CH_3 \\ | \\ HC{\cdot}OH \\ | \\ R \end{matrix} \qquad\qquad \begin{matrix} C_2H_5 \\ | \\ HC{\cdot}OH \\ | \\ R \end{matrix}$$

d-"Methyl" series. *d*-"Ethyl" series.

The simplest optically active members of the *d*-"methyl" and *d*-"ethyl" series may therefore be represented by the formulæ—

CH_3	C_2H_5
$HC{\cdot}OH$	$HC{\cdot}OH$
C_2H_5	CH_3
d-"Methyl" series.	*d*-"Ethyl" series.

In other words, the simplest member of the *d*-"methyl" series is the optical antipode of the simplest member of the *d*-"ethyl" series. The assumption which has already been made that similarity of sign in the "methyl" series always indicates similarity of configuration leads to the view that *d*-methylethylcarbinol is the simplest optically active member of the *d*-"methyl" series. Consequently, *l*-methylethylcarbinol is the first optically active member of the *d*-"ethyl" series. We therefore arrive at the apparent paradox that the simplest members of the two configuratively similar series are enantiomorophic forms of the same substance.

The earlier members of the *d*-"methyl" and *d*-"ethyl" series may be represented thus:—

CH_3	CH_3	CH_3	CH_3
$HC{\cdot}OH$	$HC{\cdot}OH$	$HC{\cdot}OH$	$HC{\cdot}OH$
CH_3	C_2H_5	C_3H_7	C_4H_9
Inactive.	*d*-.	*d*-.	*d*-.

d-"Methyl" series.

C_2H_5	C_2H_5	C_2H_5	C_2H_5
$HC{\cdot}OH$	$HC{\cdot}OH$	$HC{\cdot}OH$	$HC{\cdot}OH$
CH_3	C_2H_5	C_3H_7	C_4H_9
l-.	Inactive.	*d*-.	*d*-.

d-"Ethyl" series.

In the "ethyl" series, for the first member $R < C_2H_5$, for the second $R = C_2H_5$, whilst for the other members $R > C_2H_5$. It is therefore not surprising that there should be a change of sign in the passage from the first to the third member of this series.

The view here advanced is confirmed by reference to the curves of Pickard and Kenyon (*Trans.*, 1913, ciii., 1924, 1926, 1929). The curves in Figs. 1 and 2 for the molecular rotations of the *d*-"ethyl" series show a marked abnormality in the case of the first member. If the value for *l*-methylethylcarbinol is substituted for that of the *d*-carbinol, the curves exhibit much greater regularity. The curve (Fig. 4) for the *d*-"methyl" series shows no abnormality in the first member, for *d*-methylethylcarbinol has the same configuration as the other *d*-carbinols of this series.

Attention may also be drawn to the values for the molecular rotation of the hydrogen phthalic esters of the dextrorotatory carbinols, $C_2H_5{\cdot}CH(OH){\cdot}R$, in ethyl-alcoholic solution. The value for the rotation of the ester with $R = CH_3$ is $[M]_D + 86{\cdot}5°$, with $R = C_3H_7$, $[M]_D + 9{\cdot}42°$, whilst with $R = C_4H_9$, $[M]_D + 52{\cdot}3°$. It is evident that the value for the ester of *l*-methylethylcarbinol should be compared with those for the esters of the dextrorotatory carbinols of the "ethyl" series (compare Fig. 1, *loc. cit.*).

The temperature-coefficients for the rotations of the two series of *d*-carbinols are also of interest in this connexion. The specific rotations of the dextrorotatory alcohols of the methyl series (including *d*-methylethylcarbinol) diminish with rise of temperature (*Trans.*, 1911, xcix., 50), whereas the values for the dextrorotatory carbinols (up to ethyl-*n*-nonylcarbinol) increase with rise of temperature, with the exception of *d*-methylethylcarbinol. If the view is accepted that *l*-methylethlycarbinol is the first member of the *d*-"ethyl" series the temperature-rotation curves for the earlier members of this series are similar in character.

These considerations show the impossibility of expressing the relative configurations of a series of optically active compounds by the designations *d* and *l*.

323. "*The Surface Tension of Mixtures.* Part I. *Mixtures of partly Miscible Liquids and the Influence of Solubility.*" By Ralph Palliser Worley.

Experiments were made with the object of throwing light on peculiarities noticed in the surface tensions of weak solutions of some liquids which are only partly miscible with water.

The surface tension was measured by means of the capillary rise method, the liquids examined being aniline, phenol, and *iso*butyl alcohol. The decrease of the solubility of aniline in water produced by the addition of common salt had the effect of greatly lowering the surface tension, the final value being not far above that of pure aniline. In the case of aniline and phenol the surface tensions of some of the more concentrated solutions rose with increasing temperature, whilst the surface tensions of none of the solutions, not even the weakest, fell normally, that is, similarly to that of a pure liquid. On the other hand, the surface tension of all solutions of *iso*butyl alcohol fell regularly.

This difference of behaviour has been accounted for by the different behaviour exhibited towards water with increase of temperature. Whereas the solubility of aniline and phenol increases with rise of temperature, the solubility of *iso*butyl alcohol decreases up to 75°, and then increases rapidly until the critical solution temperature is reached. These results point to the fact, therefore, that the low surface tension of solutions of partly miscible liquids is due to the lack of solubility of the solute. The reason of this is that liquids when near their limit of solubility form solutions which are rather of the nature of colloidal than of true solutions.

324. "*The Surface Tension of Mixtures.* Part II. *Mixtures of perfectly Miscible Liquids and the Relation between their Surface Tensions and Vapour Pressures.*" By Ralph Palliser Worley.

A relation exists between the surface tension and the vapour pressure of a liquid. The object of the present research was to find out whether in mixtures of liquids deviations from a general law governing vapour pressures were accompanied by corresponding deviations in the case of surface tensions.

The following mixtures were examined:—(1) *Benzene and Ethylene Dichloride.*—The surface tensions were found to agree with those calculated from the admixture rule. So also do the vapour pressures agree with those calculated (Zawidski). (2) *Carbon Disulphide and Acetone.*—The surface tensions were found to be below the calculated values, and the curve to tend towards a minimum. The vapour pressures are much greater than those calculated, and the curve passes through a maximum. (3) *Acetic Acid and Pyridine.*—The surface tensions were much greater than those calculated, and the curve tended towards a maximum value. The vapour pressures are much below those calculated, and the curve forms a minimum.

It seems therefore that when a mixture obeys one admixture rule it obeys the other also; when the surface tensions are greater than those calculated the vapour pressures are less, and vice versa.

Additional proof was given by mixtures of benzene and carbon tetrachloride, and the homologous series of alcohols and water.

From experiments with sulphur and carbon disulphide, it appears that the relations hold good for all mixtures.

325. "*The Tautomerism of Thioanilides.*" By Percy May.

Although the thioanilides are usually represented as thioketones, $R{\cdot}NH{\cdot}CS{\cdot}R'$, yet in many respects they react as iminomercaptans, $R{\cdot}N{:}C(SH){\cdot}R'$. The methyl derivatives corresponding with both forms were prepared in the case of thiobenzanilide and thioacetanilide, and their absorption spectra were compared with those of the parent substances in the light of Thiele's theory of "conjugated" unsaturated linkings. When thiobenzanilide was sub-

jected to the action of methylating agents in neutral solvents, the sulphur was eliminated as methyl sulphide.

N-*Methylthiobenzanilide* was obtained by the action of phosphorus sulphide on methylbenzanilide, and crystallises from alcohol in small yellow cubes, melting at 90—91°.

S-*Methylthiobenzanilide* was obtained by the action of methyl sulphate on thiobenzanilide in alkaline solution, and crystallises from aqueous alcohol in colourless needles, melting at 63—64°.

326. "*The Determination of Viscosity.*" By Malcolm Percival Applebey.

In reply to the criticism of Bingham (*Trans.*, 1913, ciii., 959), the author discussed the phenomena of flow in the Ostwald viscometer and the experimental conditions requisite for obtaining accurate determinations.

327. "*Lead Cyanide.*" By Nalini Mohan Gupta.

According to Rammelsberg (D.R.P. 139456) the compound $Pb(CN)_2$ is formed by precipitating a solution of a lead salt with aqueous hydrocyanic acid or a soluble cyanide, whereas Kugler (*Annalen*, 1848, lxvi., 63) states that a basic salt, $Pb(CN)_2,2PbO,H_2O$, is formed by precipitation from an ammoniacal solution. It appears, however, to be generally recognised that the precipitate formed by the interaction of cyanides and lead salts in aqueous solution varies in composition with the concentration of the solutions employed, a fact which the author has confirmed.

Lead cyanide was decomposed by hydrogen sulphide, and the hydrogen cyanide was led into water through a U tube containing lead cyanide. To remove any traces of hydrogen sulphide from the aqueous hydrocyanic acid, some lead cyanide was added to it, and the solution shaken. As no trace of hydrogen sulphide was present no lead sulpide was formed; but after filtering this solution it was found that it contained a considerable quantity of lead. It was evident that lead cyanide, which is not appreciably soluble in cold water, is soluble in aqueous hydrocyanic acid, and it was expected that this solution would, on evaporation, deposit pure lead cyanide free from oxide.

About 250 cc. of a 5 per cent solution of hydrocyanic acid were heated to boiling with a small quantity of precipitated lead cyanide under reflux. After about half-an-hour the solution was filtered and allowed to evaporate slowly in a desiccator. The deep yellow needle-shaped crystals which separated were collected and dried in a vacuum.

Lead cyanide, even when powdered, appears to be unattacked by concentrated nitric and sulphuric acids in the cold. On adding water to a crystal, the insoluble oxycyanide is formed, and the water becomes cloudy.

A weighed quantity of the substance was heated for some hours to 120°; there was no loss in weight.

For the estimation of cyanogen and lead a weighed quantity of the substance was heated in a water-bath in a sealed tube with a weighed excess of silver nitrate and a little nitric acid. The silver cyanide was collected and weighed. The silver remaining in solution was precipitated and weighed as silver chloride, which served as a check on the weight of the silver cyanide. Finally the filtrate was evaporated with sulphuric acid, and the lead sulphate weighed. Two different samples were analysed:—

I. 0·1838 gave 0·1883 AgCN and 0·2137 $PbSO_4$. CN = 19·90; Pb = 79·42.

II. 0·2272 gave 0·2340 AgCN and 0·2638 $PbSO_4$. CN = 20·00; Pb = 79·32.

$Pb(CN)_2$ requires CN = 20·07; Pb = 79·92 per cent.

The crystals consisted therefore of lead cyanide having the formula $Pb(CN)_2$.

328. "*Contributions to the Theory of Solutions: The Intermiscibility of Liquids.*" By John Holmes.

The relative solubilities of liquids have been correlated with their molecular volumes as ascertained by a method (previously described) based on the deviations observed in the additive relations of mixtures of liquids.

On the assumption that a pure liquid consists of a collection of like spherical molecules, it is deduced that any liquids, the molecular spheres of which have equal radii, should be miscible in all proportions. In binary mixtures this mutual miscibility continues until the ratio of the respective radii reaches 1·618, when the border line of partial miscibility is reached. When the ratio is greater than this value, the mixture separates into layers, in each of which the distribution of molecules is dependent on the further change in this ratio until it reaches 2·414, beyond which the liquids should be immiscible.

The curves of volume change calculated from densities available for various mixtures of liquids have been drawn, and the molecular volumes deduced from the ascertained complexities are compared with those required theoretically, on the above hypothesis, for their relative solubilities. The molecular complexities found for these liquids differ from those generally accepted, but the corresponding molecular volumes approximate closely to solubility requirements, and render it probable that the intermiscibility of liquids is a function of molecular volume and independent of chemical constitution.

The experimental data include densities at 15° of mixtures of *iso*butyric acid with water, ethyl tartrate with water, and ethyl tartrate with glycerol; also densities at 25° of mixtures of chloroform with *n*-amyl alcohol and acetone. The critical temperatures of solution were determined for nicotine and water, and for carbon disulphide and ethyl tartrate when mixed in the proportion of 1 to 2 molecules (liquid) respectively. Volume changes in aqueous ethyl alcohol mixtures are compared with the corresponding differences from the theoretical values for refractive indices.

329. "*A Contribution to the Study of the Constitution of the Methyl Pentoses.* Part I. *The Synthesis of an* i-*Methyl Tetrose and an* i-*Methyl Tetritol.*" By Robert Gilmour.

An account was given of the isolation of an inactive *methyl tetrose* by reducing dihydroxyvalerolactone with sodium amalgam in acid solution. The free sugar has been prepared, and found to be a strongly reducing pale yellow syrup.

Methyl tetrosazone forms pale yellow needles, melting at 140—142°. *Methyl tetrosephenylbenzylhydrazone* forms colourless needles, melting at 99—100°. It was shown that the reduction of dihydroxyvalerolactone yields as the main product a *methyl tetritol*, along with only a small amount of the tetrose. The *tetrabenzoyl* derivative of methyl tetritol melts at 136—137°. In addition the methyl tetritol has been oxidised by Fenton's method to the methyl tetrose, which was isolated in the form of the phenyl benzylhydrazone.

A racemic *brucine* salt of the *methyltetronic acid* was also described (m. p. 180—181°) as well as a *dimethoxyvalerolactone* (m. p. 59—60°), which was obtained by methylating dihydroxyvalerolactone.

Further, an account was given of a method which it is proposed to adopt for the preparation of other methyl tetroses, and their importance as a means of determining the constitution of naturally occurring methyl pentoses was indicated.

Solubility in the Solid State of Nitrates, Sulphates, and Carbonates at High Temperatures.—M. Amadori.—The solubility of sulphates, carbonates, and nitrates in the solid state is either very small or negligible in the cases of the lithium, sodium, and potassium salts. The nitrates crystallise with the carbonates, and with the sulphates in eutectics constituted almost exclusively of nitrate at a temperature only 3—10° lower than that of the solidification of the nitrate. No compounds are formed either at the temperature of solidification nor at a lower temperature between sulphate and nitrate, nor between carbonate and nitrate.—*Atti Reale Accad. Lincei*, 1913, xxii., No 7.

NOTICES OF BOOKS.

A Dictionary of Applied Chemistry. By Sir Edward Thorpe, C.B., LL.D., F.R.S. Assisted by Eminent Contributors. Revised and Enlarged Edition. Vol. V. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1913

This volume, covering Sodium—Z, brings to an end the last edition of Thorpe's Dictionary of Applied Chemistry. It fully maintains the high standard of excellence which the previous volumes have reached, and contains a number of lengthy articles by authors of world-wide fame. These include, to mention only a few, articles on Spectrum Analysis, by Prof. E. C. C. Baly; on Soils, by Dr. A. D. Hall; Synthetic Drugs, by Dr. Virgil Coblenz; Vegeto-alkaloids by Prof. W. R. Dunstan; Vat Dyes, by Dr. E. Knecht; Water, by Dr. P. F. Frankland; and Terpenes, by Sir W. A. Tilden.

The Progress of Scientific Chemistry in Our Own Times. By Sir William A. Tilden, F.R.S., D.Sc.(Lond.), Sc.D.(Dub.), D.Sc.(Vict.), LL.D.(Birm.). Second Edition. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1913.

The author of this book was confronted with a very difficult task when he was called upon to deliver a short course of lectures to working men, and chose as his subject the progress of chemistry from 1837 to 1897. However, he proved to be more than equal to the occasion, and this book, based upon the lectures, is a triumphant witness to his skill in making a highly technical and somewhat obscure subject clear to readers who cannot be supposed to possess more than a slight acquaintance with the elements of chemistry. In the second edition, while the matter has been brought up to date, the general plan has not been in any way altered, and the book will give the student and the general reader a clear idea of the growth of modern chemical theory.

A Treatise on Chemistry. By Sir Henry Roscoe, F.R.S., and C. Schorlemmer, F.R.S. Volume II. *The Metals.* New Editions. Completely Revised by the Right Hon. Sir Henry Roscoe and others. London: Macmillan and Co., Ltd. 1913.

The general plan and arrangement of the original edition of this well-known standard treatise have been preserved in the fifth edition, but the whole has undergone a careful revision. Mr. T. V. Barker has made alterations and additions in the chapter on crystallography, and Dr. Makower deals with recent important researches in radio-activity, while other specialists have rendered assistance to the author in revising and amplifying the text in accordance with modern knowledge.

A Text-book of Physics. By J. H. Poynting, Sc.D., F.R.S., and Sir J. J. Thomson, O.M., M.A., F.R.S. Volume I. "Properties of Matter." Sixth Edition. London: Charles Griffin and Co., Ltd. 1913.

The fifth edition of this treatise on physics was issued only a very short time ago, and hence in the sixth edition it has not been found necessary to make any alterations beyond the addition of several important notes. In many respects it is a model text-book for students who, while possessing an elementary knowledge of physics, have not yet reached the stage when they can profitably attack advanced treatises. The text is remarkably clear and the authors' explanations are both lucid and graphic.

Carbon Dioxide Snow. By J. Hall-Edwards, L.R.C.P., F.R.S. (Edin.), Hon. F.R.P.S. London: Simpkin, Marshall, Hamilton, Kent, and Co., Ltd. 1913.

The author of this little book has done much to render the application of carbon dioxide snow more practicable and economical, and he has had much experience in using it therapeutically. He describes at some length the apparatus employed, and points out the many advantages which the snow possesses over liquid air in dermatology. He also discusses the results produced in the case of different diseases of the skin, &c., and gives a very impartial account of the effects of treatment with the snow. Details of methods of application are included, with illustrations, and allusion is made to all the necessary precautions in handling the material and in after treatment.

The Silicates in Chemistry and Commerce. By Dr. W. Asch and Dr. D. Asch. Translated by Alfred B. Searle. London: Constable and Co., Ltd. 1913.

This book is based on a thesis submitted to the University of Göttingen, and there awarded a prize in 1903 in connection with the Benek Bequest. The thesis has been much enlarged by the insertion of additional confirmatory material, and the translator has also added many explanatory or critical notes. The authors began their thesis with a comprehensive survey of the existing theories concerning the alumino-silicates, and succeeded in showing that all such theories were incompatible with the facts, except one, viz., that the alumino-silicates are complex acids or salts. Although objections can be brought forward to this view, it seemed not improbable that they are only apparent, and the authors claim that their hypothesis regarding the union of the atoms in the anhydrides of the alumino-silicates satisfactorily meets all criticisms. The theory of hexite and pentite rings (rings containing six or five aluminium or silicon and oxygen atoms) is explained, and its application not only to alumino-silicates but also to other complex acids, *e.g.*, molybdic and tungstic acids, is worked out in detail. The constitutions of clays, ultramarines, Portland cements, glasses, &c., are explained on the basis of the theory. The bearing of the hexite-pentite theory on the question of the constitution of the atom and its extension to a stereo chemical theory are also discussed, and the authors' hypothesis is undoubtedly very ingenious and requires careful consideration.

Cement, Concrete, and Bricks. By Alfred B. Searle. London: Constable and Co., Ltd. 1913.

This book contains an excellent account of the chemistry of the manufacture of cements, concretes, and bricks. The genetic relations between these three classes of building materials are clearly pointed out, and modern theories regarding the chemical and physical changes which occur in the setting and hardening of cements and the drying and burning of bricks are discussed. The author's knowledge of the scientific aspects of the brick industry and the questions involved in it is unique, and he places his experience and his wide knowledge freely at the disposal of his readers. The book is not intended for the unscientific man, and a good grounding in chemistry is required in order that it may be used profitably; it contains many suggestions as to the directions in which fruitful research may be undertaken. Methods of performing tests on concretes and cements and the making of special kinds of bricks are described in detail.

The Employment of Sodium Bisulphite in the Preparation of Plantation Rubber. By C. Beadle, H. P. Stevens, and S. Morgan.

This pamphlet contains an article which has been reprinted from the *Indiarubber Journal* for August 2nd, 1913. The authors describe shortly the tests they have performed with many specimens of rubbers prepared with and without sodium bisulphite; these tests show that on the whole the former are of slightly better quality. Hence the authors consider that the bisulphite should be regarded as a cheap and effective agent for preserving the pale colour of rubber. They have observed that rubbers prepared with sodium bisulphite tend to dry more slowly than other specimens.

The Journal of the Alchemical Society. Vol. II., Part VII. London: H. K. Lewis.

THE November number of the *Journal of the Alchemical Society* contains an interesting paper which was read by Mdme. de Steiger at the General Meeting. The subject of the paper was "The Hermetic Mystery," and Mdme. de Steiger proved herself to be an able exponent of her theory concerning the true aims of the Royal Art of Alchemy. A short abstract is also given of the discussion which followed the paper.

The British Empire Universities Modern English Illustrated Dictionary. Revised under the Chief Editorship of EDWARD D. PRICE. London, Toronto, New York: The Syndicate Publishing Co., 1914.

THIS dictionary is very much more than a mere catalogue of words and their meanings, and it may safely be used to give reliable and up-to-date information upon a great variety of subjects. The words given in the dictionary proper have been carefully chosen for utility and general information; plain rules for pronunciation are given, and the definitions are always precise and perfectly clear. In addition, there is a lengthy article on the principles of English Grammar, and Sir Arthur Quiller-Couch contributes a short history of English literature. Complete glossaries of the terms used in certain sports have been compiled for the dictionary by well-known specialists, and there are also lists of synonyms, antonyms, foreign words and phrases, contractions and abbreviations, famous characters in prose and poetry, &c. The book is printed in excellently clear type and is well bound. The illustrations appear to be its least satisfactory feature. Thus, for example, from the plate showing different breeds of dogs the pug would seem to be about the same size as the collie, and the "up-to-date barn" houses a number of cows, although a barn is correctly defined.

The Freezing-point Lowering, Conductivity, and Viscosity of Solutions of certain Electrolytes in Water, Methyl Alcohol, Ethyl Alcohol, Acetone, and Glycerol, and in Mixtures of these Solvents with one Another. By HARRY C. JONES and Collaborators. Washington, D.C.: The Carnegie Institution. 1913.

IN this monograph the continuation of the experiments which have been in progress in the Chemical Laboratory of the Johns Hopkins University during the last twelve years is described in detail, and the book may be regarded as a supplement to No. 80 of the Publications of the Carnegie Institution of Washington. Full accounts are given of the experimental work which has been done by the various collaborators, each of whom has devoted himself for periods ranging from one and a-half to two and a-half years to the elucidation of one or two questions. The results obtained in the different series of researches are also discussed in relation to one another, and some important general conclusions are drawn, especially as regards the conductivity of the dissolved electrolyte and the viscosity of the pure and mixed solvents. The work included a particularly interesting series of systematic investigations of the properties of solutions in glycerol.

Tabelle der wichtigsten Organischen Verbindungen geordnet nach Schmelzpunkten. ("Index of the Most Important Organic Compounds Arranged in Order of their Melting-points"). By Dr. RICHARD KEMPE. Braunschweig: Friedrich Vieweg und Sohn. 1913. (Mk. 8.80).

THERE are some novel features about this index which will commend themselves to those who are in the position of frequently wanting to identify organic compounds as rapidly and easily as possible. The book contains a list of some 2500 organic compounds of scientific or technical importance arranged in order of increasing melting-point, the temperatures ranging from -184° to $+419^{\circ}$, and it is claimed that in nearly all cases a determination of the melting-point will enable the chemist to ascertain the formula of the substance under investigation. For each substance the boiling-point, colour, and abbreviated constitutional formula are tabulated; also a reference to the original article in which the substance was described and to Beilstein's Tables. In cases in which different melting-points have been stated for the same compound an attempt has been made to estimate the relative value of the data and to give the temperature which is most probably correct, while if it is impossible to decide between two or more they are both given, with cross references. From this short description the great usefulness of the book will at once be recognised, particularly in cases in which only small quantities of a substance are available for identification and an elementary analysis is impossible.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clvii., No. 21, November 24, 1913.

Alkylation of Thujone and Isothujone using Sodamide.—A. Haller.—The alkylation of thujone in presence of sodamide stops at the disubstituted product, this ketone, like menthone, being incapable of trimethylation. Like menthone the ketone will give a triallyl derivative. Although isothujone does give dimethyl and monoallylisothujone, it yields chiefly condensation products. From these experiments it appears that thujone contains the group $\overset{|}{-CH}-CO-CH_2$ and isothujone the group $\overset{||}{-C}-COCH_2$.

Hydrates of Silver Fluoride.—A. Guntz and A. A. Guntz, jun.—When a neutral solution containing 120 grms. of AgF in 100 grms. of water is slowly evaporated at 10° $AgF.4H_2O$ separates out. Below 18.5° this is the only fluoride stable in neutral solution. When it is strongly supersaturated it may deposit cyrstals of $AgF.2H_2O$. If a solution containing 170 grms. AgF to 100 grms. of water is allowed to evaporate between 18° and 38° the hydrate $AgF.2H_2O$ separates in deliquescent crystals. After adding crystals of $AgF.H_2O$ to a saturated neutral solution of AgF and evaporating between 26° and 36° octahedra of $AgF.H_2O$ are obtained. In the same conditions at the ordinary temperature crystals of $3AgF.5H_2O$ may separate. These two last hydrates are unstable and readily give the anhydrous fluoride, which is also obtained by drying any of the preceding hydrates *in vacuo* over sulphuric acid.

No. 22, December 1, 1913.

This number contains no chemical matter.

Atti della Reale Accademia dei Lincei.
Vol. xxii. [ii.], No. 8, 1913.

Chemical Action of Light.—G. Ciamician and P. Silber.—When acetone, cyclohexanone, and its three methyl derivatives and methylheptenone are exposed to light in the presence of oxygen, the latter attacks the molecule in the same way as in the hydrolysis which accompanies the process of autoxidation, except in the cases of methylheptenone, which is not hydrolysed in light, and of acetone. With heptenone the autoxidation can be represented by the following scheme:—

$$(CH_3)_2C.CH.CH_2.CH_2.CO.CH_3 \rightarrow$$
$$(CH_3)_2COH.CHOH.CH_2.CH_2.CO.CH_3 \rightarrow$$
$$(CH_3)_2COH.CO.CH_2.CH_2.CO.CH_3 \rightarrow$$
$$CH_3.COCH_3 + COOH.CH_2.CH_2.CO.CH_3 \text{ (levulinic acid)}.$$

Formation of Compounds of Fluorides, Chorides, and Carbonates of Metals.—M. Amadori.—Of the couples $NaF-Na_2CO_3$, $KF-K_2CO_3$, $NaCl-Na_2CO_3$, $KCl-K_2CO_3$, only the second gives a compound in equi-

molecular proportions on the solidification of the mixed melt. Fluorides and sulphates of both potassium and sodium form stable compounds in equimolecular proportions, and thus the formation of compounds is influenced both by the nature of the acid and that of the base. Chlorides and carbonates give no compounds but simply eutectics.

MISCELLANEOUS.

Method of Disintegrating Metals and their Oxides into a Colloidal State.—Masamichi Kimura.—When a piece of metal heated in a Bunsen burner or by an electric current is suddenly introduced into water a number of fine particles is produced. A few drops of distilled water were first examined with the ultramicroscope and found to contain no colloidal particles. A piece of platinum wire was heated to a white heat by an electric current and put into the water; this process was repeated, and a drop of the water was then examined under the microscope, when many fine particles showing the Brownian movement were observed. From the investigation of the cataphoresis it was found that some particles travelled towards the cathode while others proceeded in the opposite direction. Similar experiments with silver and copper gave the same results.—*Memoirs of the College of Science and Engineering, Kyoto Imperial University*, 1913, v., No. 6.

Lawes and Gilbert Centenary Fund.—During the Christmas holidays the Lawes and Gilbert Centenary Fund Committee ceased work so as not to interfere with the ordinary Christmas appeals; it has now begun work again to collect the last £1600 needed to complete the scheme. The object of the Centenary Fund is to build and equip a satisfactory laboratory for the prosecution of researches in agricultural chemistry, a subject largely founded on the experiments of Lawes, who was born just 100 years ago, and of Gilbert, who was born three years later. These investigators founded the Rothamsted Experimental Station, the oldest and for many years the best equipped agricultural experiment station in the world. Rothamsted has maintained its high position in respect of its staff and its field plots, but it has fallen behind in laboratory accommodation, and a serious effort is now being made to remedy this defect. The Committee has ascertained that a satisfactory laboratory can be erected and equipped for £12,000, and it has decided to collect the money, and to put up the laboratory this year in commemoration of the centenary of the birth of the founders. Its efforts have been so far successful that only £1600 is now required, and an urgent appeal is addressed to all interested in agricultural science to aid the Committee in closing the list so that the work can be put in hand at an early date. Subscriptions should be sent to the Secretary, Rothamsted Experimental Station, Harpenden, Herts.

Royal Society of Arts.—The Swiney Prize.—The Swiney Prize for Jurisprudence has been awarded to Mr. John W. Salmond, K.C., Solicitor General for New Zealand, for his work "Jurisprudence." The prize consists of a sum of £100 contained in a silver cup of the same value. It was founded in 1844 under the will of Dr. George Swiney, a somewhat eccentric medical man, who left £5000 Three per cent Consols to the Society in order that the prize might be awarded on every fifth anniversary of his death to the author of the best published work on Jurisprudence. Although the bequest was made to the Society of Arts alone, Dr. Swiney appointed as adjudicators the members of the Society and the Fellows of the Royal College of Physicians. An arrangement was made by the adjudicators that the award should be given alternately for Medical and General Jurisprudence. The cup is made after a design prepared in 1849, for the first award, by Daniel Maclise, R.A., and the execution has been entrusted to Messrs. Garrard. The prize has been awarded on thirteen previous occasions, among the recipients being Sir Henry Sumner Maine, K.C.B., D.C.L., for his "Ancient Law"; The Rt. Hon. Sir Robert Joseph Phillimore, D.C.L., for his "Commentaries on International Law"; Thomas Erskine Holland, D.C.L., for his "Elements of Jurisprudence"; and Sir Frederick Pollock, Bart., and Professor F. W. Maitland, for their "History of English Law before Edward the First." It may be mentioned that in addition to this bequest to the Royal Society of Arts, Dr. Swiney also left a similar sum of £5000 to the Trustees of the British Museum for the establishment of a lectureship in geology.

New Catalogue. — Messrs. Crosby Lockwood and Son (7, Stationers' Hall Court, Ludgate Hill, and 5, Broadway, Westminster), have recently issued a new catalogue of the Scientific, Technical, and Industrial books published by them. The catalogue, which is well illustrated, contains extracts from some book reviews, and Messrs. Crosby Lockwood and Son will be pleased to send it post free to any readers of the Chemical News who may desire it.

Literary Intelligence.—Messrs. J. and A. Churchill have just ready for publication Volume VIII. of the new edition of "Allen's Commercial Organic Analysis." This volume has been re-written under the editorship of Mr. W. A. Davis, B.Sc., and Mr. S. S. Sadtler, S.B. The subjects and authors are as follows:—"Enzymes, Proteins of Plants," by E. Frankland Armstrong; "The Proteins and Albuminoid Substances, Digestion Products of the Proteins," by S. B. Schryver; "Proteins of Milk," by L. L. Van Slyke; "Milk," by H. Leffmann; "Milk Products," by C. Revis and E. R. Bolton; "Meat and Meat Products," by W. D. Richardson; "Hæmoglobin and its Derivatives," by J. A. Gardner and G. A. Buckmaster; "Albuminoids or Scleroproteins," by J. Alexander; "Fibroids," by W. P. Dreaper. It will be observed that each contribution is dealt with by an expert in his department.

MEETINGS FOR THE WEEK.

Monday, 26th.—Royal Society of Arts, 8. (Cantor Lecture). "The Relation of Industry to Art," by Sir Charles Waldstein, Litt.D., Ph.D.

Tuesday, 27th.—Royal Institution, 3. "Animals and Plants under Domestication," by Prof. W. Bateson, F.R.S., &c.

Wednesday, 28th.—Royal Society of Arts, 8. "Japanese Colour Prints," by Edward F. Strange, R.E. (Hon.).

Thursday, 29th.—Royal Institution, 3. "The Mind of Savage Man," by W. McDougall, F.R.S.

— Society of Dyers and Colourists, 8. "Effects of Mineral Loading upon the Physical Qualities of Hedychium Paper" and "Tests to Determine the Relative Strength and Elasticity of some Natural Fibres," by C. Beadle and H. P. Stevens.

— Royal Society. "Origin of Thermal Ionisation from Carbon," by O. W. Richardson. "X-ray Spectra given by Crystals of Sulphur and Quartz," by W. H. Bragg. "Temperature Variation of the Photo-elastic Effect in Strained Glass," by L. N. G. Filon. "Studies in Brownian Movement—I., Brownian Movement of the Spores of Bacteria," by J. H. Shaxby and E. E. Roberts. "Transmission of Cathode Rays through Matter," by R. Whiddington. "Variation with Temperature of the Specific Heat of Sodium in the Solid and the Liquid State; also a Determination of its Latent Heat of Fusion," by E. Griffiths. "Radiation from a Gas," by G. Green. "Similarity of Motion in relation to the Surface Friction of Fluids," by T. E. Stanton and J. R. Pannell. "Influence of Molecular Constitution and Temperature on Magnetic Susceptibility," by A. E. Oxley. "Boiling-point of Sulphur on the Thermodynamic Scale," by N. Eumorfopoulos.

Friday, 30th.—Royal Institution, 3. "The Foundations of Diplomacy," by H. Wickham Steed.

Saturday, 31st.—Royal Institution, 3. "Neglected Musical Composers," by Prof. F. Corder.

THE CHEMICAL NEWS.

VOL. CIX., No. 2827.

THE SOLIDIFYING AND MELTING-POINT OF MUTTON TALLOW AND ITS FATTY ACIDS.

By ROBERT MELDRUM.

THE following investigation was undertaken to ascertain the relationship between the melting point and solidifying-point of mutton tallow and its fatty acids. The thermometer bulb method was used for melting-point, and the solidifying-point by Dalican's method, both methods having been previously investigated by the author (CHEM. NEWS, cviii., No. 2813). All the readings are degrees Centigrade. The tallows are fine Australian mutton tallows.

Sample I.—Contains 0.84 per cent Free Fatty Acids.

Solidifying-point + rise.	Rise.	Melting-point.	Difference between s.-p. and m.-p.	Difference between zero and m.-p.
39.8	4.3	48.3	8.5	12.8
40.4	3.0	48.2	7.8	10.9
40.4	4.4	48.4	8.0	12.4
40.6	5.2	48.3	7.7	12.9

Fatty Acids (20.19 per cent KHO to Neutralise).

45.1	1.1	46.8	1.7	2.8
45.4	1.2	46.8	1.4	2.6
45.4	1.2	47.0	1.6	2.8
45.5	1.2	46.9	1.4	2.6

Sample II.—Contains Free Fatty Acids, 1.13 per cent.

41.2	4.8	48.4	7.2	12.0
41.6	5.0	48.0	6.4	11.4
41.4	3.8	48.4	7.0	10.8

Fatty Acids (20.19 per cent KHO to Neutralise).

47.2	1.2	47.6	0.4	1.6
47.2	1.0	47.8	0.6	1.6
47.6	1.0	47.8	0.2	1.2

Sample III.—Contains Free Fatty Acids 0.84 per cent.

44.0	4.4	50.0	6.0	10.4
44.4	5.1	50.0	5.6	10.7
44.3	4.7	50.6	6.3	11.0
44.8	5.4	50.3	5.5	10.9

Fatty Acids (20.19 per cent KHO to Neutralise).

49.2	1.2	49.8	0.6	1.8
49.3	1.1	50.0	0.7	1.8
49.6	1.6	50.0	0.4	2.0
49.5	0.9	49.8	0.3	1.2

Sample IV.—Contains Free Fatty Acids 0.43 per cent.

41.6	4.2	49.0	7.4	11.6
41.7	3.1	48.3	6.6	9.7
42.4	5.2	48.6	6.2	11.4

Sample V.—*Beef Tallow*.—Contains Free Fatty Acids 0.43.

37.2	3.4	46.6	9.4	12.8
37.8	3.6	46.3	8.5	12.1
37.2	3.6	46.4	9.2	12.8

Fatty Acids (19.48 per cent KHO to Neutralise).

42.8	0.4	43.8	1.0	1.4
42.7	0.3	44.0	1.3	1.6
42.7	0.5	43.6	0.9	1.4

The following table shows the variations in readings on all the samples, indicating the limits of accuracy of methods used as applied to tallow. It will be noted that beef tallow behaves the same as mutton:—

	Tallow. °C.	Fatty acids. °C.
Solidifying-point + rise	0.8	0.4
Rise	2.2	0.7
Melting-point	0.7	0.4
Difference between solidifying-point and melting-point	1.2	0.4
Difference between lowest T° fat cooled and melting-point	2.0	0.8

The fatty acids, therefore, yield more constant results than the tallows; the latter yielding errors of 50 per cent to 300 per cent greater than the acids. It is clear some erratic conditions are present during the setting of tallow. Such a large variation in the rise shows this more prominently.

Variation in Solidifying-point of Tallow.

This variation in solidifying-point was further investigated. A sample of tallow was selected and melted down in test-tube 7″+1″ at 60° C., fixed in apparatus, and cooled by stirring to 42° C., when thermometer was fixed in centre, 1½ inch from bottom, and allowed to cool.

Thermometer fell to..	41.7	39.7	39.8	39.3	39.6
Thermometer rose to	42.3	41.7	41.7	42.1	42.1
Rise	0.6	2.0	1.9	2.8	2.5

Twenty-four hours after another five tests gave—

Thermometer fell to..	37.5	37.8	39.1	38.7	38.8
Thermometer rose to	40.3	41.1	41.0	40.8	41.4
Rise	2.8	3.3	1.9	2.1	2.6

Variation in rise	2.7
Variation in zero	4.2
Variation in solidifying-point ..	2.0
Average rise	2.2
Average solidifying-point	41.4

The fluctuation in the solidifying-point in the above ten tests is 2.5 times greater than that recorded in the former series of tests. It will be noted the zero to which the temperature falls before rising shows the greatest variation, and it appears it is this factor which governs constancy in the solidifying-point and the "rise." The "zero" is apparently raised or lowered by the stirring, rate of cooling, or other thermal conditions. The following tests show this more clearly. Melted at 60°, cooled by stirring to the indicated temperature, then fixed thermometer.

Cooled to	50	45	40	38	36.2
Thermometer fell to..	37.4	37.6	37.8	38.7	36.2
Thermometer rose to	39.3	39.9	40.3	41.9	40.6
Rise	1.9	2.3	2.5	3.2	4.4

Variation in rise	2.5
Variation in zero	2.5
Variation in solidifying-point ..	2.6
Average rise	2.8
Average solidifying-point	40.4

The tests show that both the setting-point and "rise" increase with the speed of cooling. Theory, therefore, would require that the more rapid a tallow is cooled by means of cold water-baths or cold air, the "rise" and solidifying-point must increase; and, on the other hand, by very slow cooling in warm air or warm water-baths, the "rise" ought to be eliminated and the solidifying-point increased. Such is not the case is seen from the following experiments:—

1. Melted tallow at 60° in test-tube, cooled to 50° by stirring, then fixed in apparatus filled with water at 15°. A rapid and continuous fall takes place, but no "rise" or stationary-point was observed. This was repeated with same result. Theory would require that the latent heat of

crystallisation amounting to 4·4° ought to produce a "rise" or a "zero" point.

2. Melted at 60° in test-tube, cooled by stirring to 50°, placed in apparatus with water at 50°, and fixed thermometer. One hour in cooling and rising. Thermometer fell to 42·3; rose to 43·3. Rise = 1°. Here there is a tendency to eliminate the "rise" by slow cooling with high solidifying-point, which agrees with theory.

3. 500 grms. melted in beaker at 60°, cooled to 50° by stirring, and thermometer fixed in centre, 1" from bottom, and allowed to cool in air at 15°. At 39·8° is quite fluid and transparent, with a layer of solid fat on bottom ¼ inch thick. Thermometer falls to 39·8°; rose to 44·0. Rise = 4·2°. Here the solidifying-point is at maximum with a maximum "rise."

4. 500 grms. as above but cooled to 41° by stirring. Thermometer fell to 40·8°; rose to 45·2. Rise = 4·4°. It is seen that by varying the conditions of cooling by using air, cold water and hot water jackets, and by using large volumes of tallow, the solidifying varies by 5·9° and the "rise" by 4·4°. There is no doubt that the setting-point is affected by stirring, as when stirred the mass becomes semi-solid. No "rise" takes place till the stirring ceases, when there is an immediate rapid "rise."

Variations in Melting-point of Tallow.

A most interesting and important point is that the higher the solidifying-point the more closely does it approach the melting-point. With this particular sample the lowest melting-point obtained was 48·4°, or a difference of 3·2° between melting-point and solidifying-point. A great deal of obscurity still persists in chemical and technical literature as regards the change in molecular structure resulting from heating fats, and particularly tallow, at temperatures greatly in excess of the fusing-point. Thus Allen states in his well-known work (vol. ii., p. 21): —"It has been observed that many of the fats solid at ordinary temperatures have at least two *distinct* melting-points. Thus the ordinary tallow of commerce previously melted at a temperature considerably above its fusing-point shows fusion of 95° to 96° F. If carefully remelted at that temperature, cooled, and melting-point taken again, it will sometimes be found nearly 20° above the former." Again, he states (vol. ii., p. 22):—"In fatty acids there often is a difference of 3° to 4° C. between the two points, between incipient and perfect fusion." These opinions are still very prevalent amongst technical chemists and analysts. So far as the author's experience and observations are concerned with several hundred samples of tallow, no variation in melting-point has been observed due to temperature of melt or period of heating. The cause is more likely variations in the melting-point method used. So far as the thermometer bulb method is concerned, as applied to tallows and their fatty acids, the results are fairly constant within 0·7° and 0·4° respectively, whatever the heat treatment may be up to 100° C. The variation in melting-point due to thickness of coating of fat on bulb is as follows:—Very thin, 49·9°; thick, 48·4°; difference, 1·5°. Extra thin films on bulb would increase the apparent melting-point considerably, as only a trace of fat would flow to form a drop. The following is a record of the melting-point of this tallow by various methods:—

Melting-point of Tallow by Various Methods.

Thermometer bulb ..	48·6	48·9	49·0	= 48·4
Capillary tube	48·5	49·5	49·0	= 49·0
Test-tube	50·5			= 50·5

To ascertain what actually takes place during the melting and solidifying of the fat a test-tube, 7" × 1", half full of the solidified tallow which had been cooled for several hours, was surrounded with water-jacket and heated at the rate of 0·5° per minute during the stirring of both tallow and water in jacket.

45° C.	Opaque soft paste which can be stirred.
48	Opaque thick liquid, easily stirred.
49·5	Opaque limpid liquid.
50·0	A trace of opacity present, limpid.
50·5	Free from opacity, quite transparent.
50·0	Regains trace of opacity.
49·5	Opacity increased.
48·0	Opacity increased and thickness.
46·0	Very thick and white, semi-liquid.
44·5	Ceased to stir due to thickness; fixed thermometer; rise commences.
45·7	Thermometer rose; tallow hard. Rise, 1·2°.

It will be observed the tallow only completely clarifies at 50·5°, and with a drop of 0·5° the opacity reappears. It would therefore appear that the true melting point of the tallow is 50·5°, or nearly 2° higher than the thermometer bulb method. This question of incipient and complete fusion or the declaration of two melting-points cannot be maintained, or if admitted there must be present not two but *several* fusing-points. The actual melting-point must be that at which all trace of opacity disappears and reforms. It appears to the author that the test-tube method of determining melting-points is a very accurate one, as the conditions are under perfect control, and the melting-point based on complete clarification is well defined, and can be confirmed by cooling half a degree. Another important factor is that the fat is obtained in a fluid state, and its viscosity, opacity, and gravity, and other physical properties can be determined at a few points higher or lower than the point of clarification.

The above experiment shows there is absolute agreement between the point at which solidification commences and the actual melting-point—50·5° C. This relationship between the opacity point and the determined melting-point is a very important one, and is accountable for numerous discrepancies in published melting-points. The following experiment indicates this relationship, which likely holds good for nearly all fats, waxes, and organic compounds. Spermaceti having a melting-point by thermometer bulb method of 45·3° C., and a solidifying-point of 45·7° C. with no "rise," when maintained at 45° C. for one hour is fluid and strongly opaque; at 45·7° C. becomes transparent and free from opacity; cooled to 45·5° C. opacity reappears. So far as this test goes the opacity point is the true melting and solidifying point. To explain, therefore, why tallow and many other solid fats will only solidify several degrees below their opacity point requires further explanation.

Chemical and Physical Changes of Tallow due to Heating.

So far as the author is concerned all the available evidence supports the fact that heating for more or less prolonged periods greatly in excess of the melting point has no disturbing influence on the constancy of either point. The same holds good for rapid and slow cooling, for repeated heating and cooling. If this was not so, wide variations in the melting point would result. The fluctuations in the solidifying-point, therefore, must be due to causes other than these. The changes in molecular state, or chemical constitution, if taking place at all, must happen during the cooling down process or the change must take place at the "zero" point. The chemical change, if present, may result in a combination of the solid and liquid glycerides, or the solid glycerides may undergo partial hydrolysis into mono- and di-stearins. The mechanism of this hypothetical chemical change may be further extended without limit. Chittenden and Smith (*Journ. Chem. Soc.*, xlviii., 508) have recorded stable mixtures of di- and tri-palmitin. It is therefore probable that many double compounds may result of the solid and liquid glycerides by thermal conditions, resulting in a low variable solidifying-point with fluctuating "rises."

The most generally accepted theory as to the melting and solidifying-points of tallow and other fats varying

from the normal is isomerism. Tristearin exists in three isomeric modifications. The theory is as follows:—

α. Produced by heating tristearin to 74°. Solidifies at 51·7°, melts 52°.

β. Produced by heating α variety to 52° until it solidifies. Melting-point, 64·2.

γ. Produced by heating α to 65° or by crystallising stearin from ether. Solidifying-point, 63° C.; melting-point, 69·7°.

If the abnormal behaviour of tallow in solidifying is due to this or similar isomeric changes, or to the formation of double compounds, we would expect that by diluting the tallow with a chemically neutral solvent like mineral oil the "rise" resulting from the liberation of heat would decrease with dilution, and erratic ratios between melting-point and solidifying-point would result. Also that some erratic changes would take place by dilution with a fluid animal oil. That such is not the case will be seen from the following results:—

Solidifying-points and Melting-points of Mixtures of Tallow and Mineral Oil (sp. gr. 0·905).

Tallow. Per cent.	Oil. Per cent.	Melting-point.	Solidifying-point + rise.	Rise	Melting-point less solidifying-point.
100	0	50·0	44·2	3·2	5·8
90	10	49·0	44·3	3·2	4·7
80	20	47·1	41·8	3·8	5·3
70	30	46·3	39·2	4·2	7·1
60	40	44·7	36·5	3·5	8·2
50	50	42·7	34·4	4·4	8·3

Solidifying and Melting-points of Mixtures of Tallow and Lard Oil.

100	0	48·0	41·9	4·2	6·1
90	10	47·4	41·6	4·4	5·8
80	20	46·7	40·1	3·8	6·6
70	30	46·0	39·2	4·2	6·8

(Average of four tests for each mixture).

It is conclusive dilution does not affect the "rise" nor the ratio between melting- and solidifying-point. It is difficult to reconcile these results with the isomeric theory or chemical theory. Perhaps the data is insufficient for the formulation of any sound hypothesis, but, in the course of these and similar researches the author has been strongly impressed with the dynamic factor in crystallisation. The amount crystallised per unit of time in unit mass must affect more or less the uniformity in the "rise" and solidifying-point. The dynamic phase therefore as applied to tripalmitin, tristearin, and other glycerides may be that the speed of crystallisation is slow at the melting-point, and increases to maximum at x degrees lower. This theory would explain the opacity point, and would indicate that point as the true solidifying and melting-point. The three points would then agree together.

The Ratio between the Melting-point of Tallow and its Fatty Acids.

There is a close relationship between the melting-point of tallow and the melting-point and solidifying-point of its acids. Thus:—

	1.	2.	3.	4.
Melting-point, tallows ..	48·2	48·0	50·0	46·3
Melting-point, acids ..	47·0	47·8	50·0	44·0
Solidifying-point, acids ..	45·4	47·2	49·6	42·7

With more reliable and accurate methods for determining these points, and a clear definition and understanding of the nature of these points and more extensive data, there is indications that these differences would be reduced to a small constant and the "titre" of acids determined directly from melting-point of tallow. It is interesting to note that No. 3 tallow shows little difference in the agreement of its three factors.

The difference between the lowest temperature to which a tallow falls during solidification or its "zero" and its melting-point is apparently a constant approximating 12° or 13°, and in the fatty acids is between 2° to 4°, as will be seen from the following:—

Tallows.

	1.	2.	3.	4.	5.
Melting-point	48·4	48·4	50·6	46·6	48·4
Zero	35·5	36·4	39·3	33·6	36·2
Difference ..	12·9	12·0	11·3	13·0	12·2

Fatty Acids.

Melting-point	47·0	47·8	50·0	44·0	48·0
Zero	44·2	46·0	48·0	42·2	44·3
Difference ..	2·8	1·8	2·0	1·8	3·7

In all the observations made the tallows, it will be noted, contained free fatty acids, and therefore free glycerin, and whether small amounts of these modify the solidifying-point and is the cause of the low zeros or the erratic "rises," the author is at present investigating.

PASSIVITY.*

By GERHARD C. SCHMIDT.

(Concluded from p. 40).

6. *Proof that a Metal is rendered Active by Diffusion of Hydrogen Ions.—Iron.*

In order to transform passive iron into the active condition by diffusion of hydrogen, advantage was taken of the discovery of Grave (*loc. cit.*, p. 570) that when hydrogen is liberated at one side of a piece of iron foil, it rapidly diffuses through and alters the e.m.f. The arrangement of the apparatus was as follows:—A and B are two glass troughs, one side of each having been removed and replaced by a thin sheet of iron, Fe. P is a platinum cathode connected with two accumulators. The iron is earthed. The two troughs are filled with dilute potassium

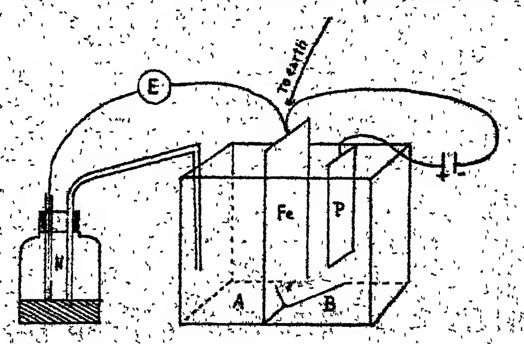


FIG. 1.

hydroxide, which has a slight passivating action. N is the normal electrode. The p.d. between the iron and the normal electrode is measured by means of a sensitive Dolezalek electrometer, E. The alkali renders the metal passive, and it was anticipated that when hydrogen is liberated on one side of the iron the gas will pass through by diffusion and render the iron active. The result of an experiment is shown in Fig. 2, the times being represented as abscissæ and the e.m.f.'s as ordinates. The letters H and O indicate the moment when the liberation of these gases began. The rapidity with which the hydrogen acts

* A Contribution to the General Discussion on "The Passivity of Metals" held before the Faraday Society, November 12, 1913. Experimental Part by W. RATHERT.)

is remarkable. The commencement of its evolution is followed almost instantly by alteration of e.m.f. on the other side.

The investigations did not, however, lead to conclusive results; the iron remained active under all circumstances. The probable reason is that the amount of hydrogen which passes through is too small to counteract the passivating action of the potassium hydroxide. The solution in the trough A was therefore replaced by another electrolyte, chromic acid. The latter is a strong oxidising

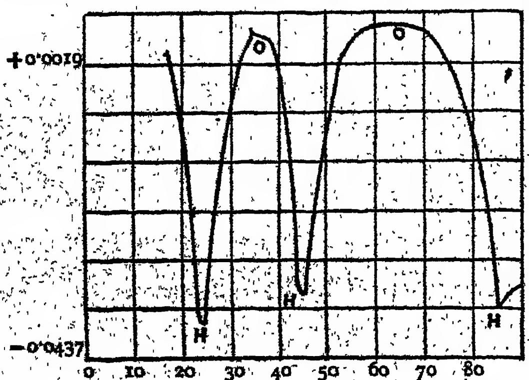


Fig. 2.

and passivating agent as well as an acid. If the hydrogen theory is correct and the iron is highly charged with hydrogen, it ought to be possible so to oppose the two properties of chromic acid that one of them prevails. Preliminary investigations showed that in chromic acid any potential through a wide range can be imparted to iron. The more concentrated the solution the more

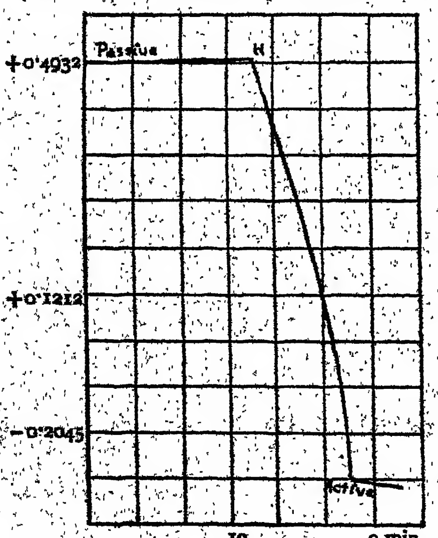


Fig. 3.

positive (more noble) is the potential; the more dilute the solution the less noble is the potential. If an acid is chosen the concentration and oxidising power of which is just sufficient to render the iron passive, it should be possible to render the metal active by hydrogen reaching it by diffusion. The result of such an investigation is represented in Fig. 3, which shows that the iron is at first passive, but the moment that hydrogen begins to be liberated (at H) the potential falls very rapidly and the metal becomes active. If the evolution of hydrogen is now interrupted (in the second figure B) the metal remains active and dissolves with evolution of hydrogen.

Quantitative investigations showed that more iron is dissolved than corresponds with Faraday's law. This is not surprising, since iron not only goes into solution according to the law in question, but is also acted upon directly by chromic acid. This behaviour is analogous to that of a zinc electrode in sulphuric acid; more zinc is dissolved than corresponds with Faraday's law unless the metal is protected by amalgamation against the direct attack of the acid.

These results, in combination with the above theoretical considerations, are practically conclusive in favour of the hydrogen theory. On the basis of the oxide theory, however, it might be supposed that the metal under the action of the acid becomes coated with oxide

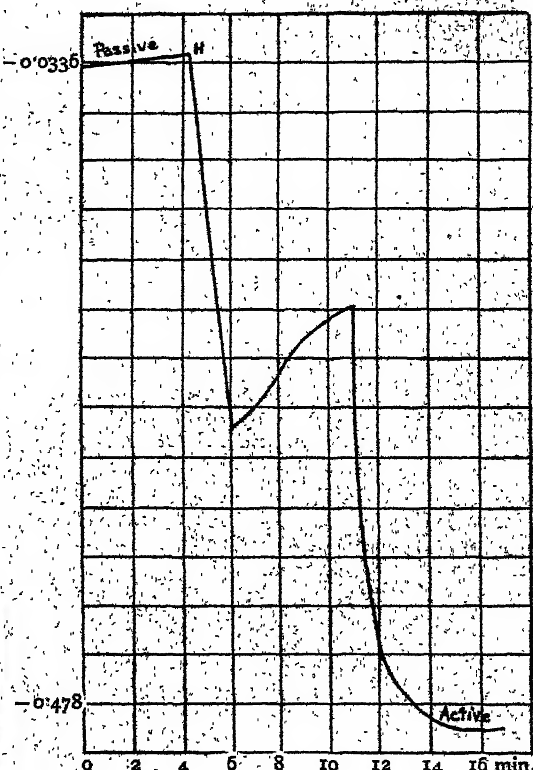


Fig. 4.

which is reduced by the hydrogen so that the electrode again becomes active. To this it might be objected that passive iron remains quite bright in chromic acid. Further, if a layer of oxide is formed at first there would appear to be no reason why this process should not continue. This, however, is not the case, since, as was shown above, when the metal is activated by means of hydrogen it continues active even when the evolution of hydrogen is interrupted. The latter fact can readily be accounted for on the hydrogen theory as follows:—When iron is in process of being dissolved and is passivated at certain points by the chromic acid, local currents are immediately set up and the passive regions again become active under the influence of the liberated hydrogen.

Moreover, according to the oxide theory, iron in chromic acid should be rendered active by rupture of the surface film by scratching, which is not the case. Further, an oxide of definite composition, such as is presumably

postulated in this case, should show a definite potential, whilst it was found that iron in chromic acid shows all possible potentials, depending on the concentration of the acid.

All these results and arguments constitute so powerful support to the hydrogen theory as to put its validity practically beyond question, more particularly as the most delicate methods have failed to detect a trace of the hypothetical oxide.

7. *Chromium.*

The successful results obtained in the activation of passive iron by diffusing hydrogen induced me to make analogous experiments with chromium. The metal was electrolytically deposited on thin sheets of iron or steel. After about fourteen days the initially active metal became

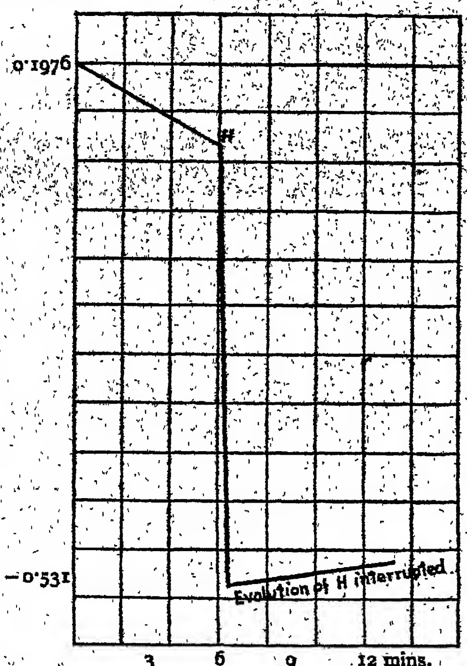


Fig. 5.

passive—probably owing to gradual loss of hydrogen. The experiments were made as described above. The results are given in the accompanying table and are represented graphically in Fig. 4.

Table I.

(Chromium deposited on Steel and allowed to stand Fourteen Days in 0·1/N Sulphuric Acid exposed to the Air).

Potential.	Time. Min.	Evolution of Gas.
−0·0336	0	
−0·0262	4	
−0·3059	6	Hydrogen
−0·2909	7	"
−0·2321	9	"
−0·2174	11	"
−0·4310	12	"
−0·4530	13	"
−0·4780	14	"

The chromium electrode was at first passive. Under the influence of the diffusing hydrogen the potential fell at first rapidly, then more gradually till it reached a value of −0·2174 volt and finally fell within a minute to −0·4310 volt. The electrode was then active, as shown by the fact that it began to dissolve with a vigorous evolution of hydrogen, and it continued active when the cathodic polarisation was interrupted. Of the other experiments, which gave analogous results, only one is quoted, as it shows the rapidity of action of the hydrogen.

Table II.

(Chromium deposited on a Steel Foil 0·08 mm. thick. Electrolyte 0·1/N H_2SO_4).

Potential.	Time. Min.	Evolution of Gas.
−0·1976	0	
−0·2232	3	
−0·2488	6	
−0·5310	6·5	Hydrogen
−0·5310	7·5	
−0·5246	8·5	
−0·5112	13·5	

The results are represented in Fig. 5. The electrode was originally passive; within half a minute of the commencement of the evolution of hydrogen it became active and began to dissolve with rapid evolution of gas. The dissolution continued after interruption of the cathodic polarisation till all the chromium had disappeared.

Conclusion.

In the foregoing a series of observations have been described which in our opinion cannot be explained on the oxide theory, but are in best accord with the hydrogen theory. The views of the author on the phenomenon of passivity have already being briefly described by Grave. Just as water or other liquids do not boil, even when their vapour pressure is equal to that of the superincumbent pressure, unless a catalyst such as air is present, so the metals which can be passivated dissolve *rapidly* only in the presence of a catalyst. The most important of such catalysts is hydrogen, since it is dissolved readily and in large amounts by metals. Whether other gases are also catalytically active cannot at present be stated, since they are only absorbed to a very small extent by metals. Just as relatively small amounts of air initiate rapid evaporation in large quantities of liquid, so a small quantity of hydrogen can activate large amounts of iron, nickel, and chromium. It might be supposed that the hydrogen, like air in the case of boiling, forms a nucleus round which the ions of metal collect. Further investigation must decide whether this hypothesis is in accord with the facts.

THE SCIENTIFIC WEEK.

(From Our Own Paris Correspondent).

The Progress of the Electro-Metallurgical Industry.

Some very interesting facts with regard to the progress of modern science in electro-chemistry and electro-metallurgy have just been established by M. Gall, the new President of the Society of Civil Engineers. These two forces have been recently placed at the disposal of technical labour at a price hitherto unknown for metals or alloy, the demands for which increase day by day. M. Gall, on taking the chair at the recent Meeting of Civil Engineers, reviewed the principal industries, electro-chemistry and electro-metallurgy. He drew attention to the remarkable development of these two scientific discoveries during the last thirty years. The electrolytic refining of copper only produced at first 20 tons of electrolytic-copper per day; that is to say, 4 per cent on the total consumption. In 1910, thirty-eight factories refined 469,000 tons of copper, representing 55 per cent on the entire production. "J. B. Dumas," said M. Gall, "has preserved for us the souvenir (in an anecdote of Faraday) of the emotion felt by that great Professor of Chemistry when he saw the first globule of alkaline metal

appear, by the influence of the pile that the hand of man had ever isolated." "Experience capitale" is the title given by Davy to this experiment on the register preserved at the Royal Society. The fabrication of soda since these researches has developed considerably. As to aluminium discovered by Henri Sainte-Claire Deville, the entire production is more than 50,000 a year, and the production in France alone is more than 15,000 tons. The uses of the electric furnace are numerous. "Ferro-silicon" and the "ferro-chromium" are manufactured by millions of tons. The production of electric steel is more than 120,000 tons a year. Lastly, carbide of calcium is an important production of the electric furnace. In the whole world these are more than 300,000 tons of carbide of calcium manufactured yearly, and out of that France manufactures 36,000 tons. A recent and very important application of the electric furnace is the production of nitrogenous manure, drawn from atmospheric nitrogen. Sir W. Crookes pointed out that the increase in the white races entails an augmentation of many necessary cereals, which must be extensively cultivated to satisfy the demand. It is proved that Germany (which only produces two-thirds of the corn necessary for its consumption) could increase the cultivation 4,000,000 tons, by using 130 kilogrms. of manure per hectare. Statistics go to prove that during the present century the beds of nitre in the mines of Chili will become exhausted—according to some in the year 1940 and to others in the year 2032. The production direct of nitrates is to-day an accomplished fact. At the present moment 160,000 tons of calcium cyanamide are manufactured, which corresponds to 30,000 tons of nitrogen. Other methods furnish about 160,000 tons of nitrate of lime, and this is only the commencement. For the whole of France the statistics value the force of industrial motors at 3,144,000 horse-power, and of those of railways and tramways at 10,309,000 horse-power. We arrive thus at a necessary force of 50 milliards, 700 millions of horse-power hours. The hydro electric force of France is, according to M. Gall, equal to a tenth of this amount. It could immediately be increased 50 per cent by the utilisation of two electromotive forces, that of the Rhone and that of the Durance. The utilisation of each of these forces corresponds to the discovery of coal-beds producing, one 1,800,000 tons, the other 80,000 tons of coal a year.

To Receive the Signals of the T.S.F.

M. Bigourdan, astronomer of the "Observatoire," presented to the Academy a paper from MM. Tauleigne, Ducretet, and Roger on a new system for registering on a Morse-receiver wireless telegraphy signals, which are generally transmitted by telephone. This method comprises a "detector electrolytique à réglage," combined with the use of a magnetic polarising relay. The three experimentists have been able to register signals at a distance of 150 and 170 kilometres by means of a rod 12 metres long, held to a height of 12 metres from the ground.

Action of Alkaline Sulphites on Acetylenic Acids and their Ether Salts.—E. Lasausse.—Neutral alkaline sulphites act on free phenyl propiolic acid to give the neutral salt of a β-sulphocinnamate. Sodium disulphite reacts with methyl phenylpropiolate to give the cinnamate of methyl monosulphonate of sodium and the phenylpropionate of methyl disulphonate of sodium. Methyl amylpropionate fixes 2 molecules of sodium disulphite with formation of the saturated disulphonic derivative, $C_5H_{11}—C_2H_2(SO_3Na)_2—CO_2CH_3$. Thus it is possible to attach 1 or 2 molecules of an alkaline disulphite to the salts and ether salts of acetylenic acids of general formula $R—C\equiv C—CO_2H$. In the first case the product is the alkaline salt of a monosulphonic acid with an ethylene bond; and in the second case the alkaline salt of a saturated disulphonic acid.—*Bull. Soc. Chim. de France*, 1913, No. 18-19.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, December 18th, 1913.

Prof. W. H. Perkin, LL.D., F.R.S., President, in the Chair.

Reference was made to the death, on December 4, 1913, of Mr. Christer Peter Sandberg, of Westminster, who was elected a Fellow on March 3, 1870.

Messrs. H. F. Tayler, A. O. Blackhurst, V. Lefebure, C. J. Dickenson Gair were formally admitted Fellows of the Chemical Society.

Certificates were read for the first time in favour of Messrs. Ethelbert William Blair, B.Sc., 70, Fountayne Road, Stoke Newington, N.; Richard Charles Denington, 69, Dover Road, S. Wanstead, N.E.; John Garth, 170, St. Thomas's Road, Preston; Ivan Richard Gibbs, B.A., University Hall, 3, Moors' Gardens, Chelsea, S.W.; Theophilus Harper, 39, Camden Street, Belfast; William Pawson Robson, B.A., Ph.D., 78, Rolland Street, Cape Town; Chandra Bhusan Roy, M.A., Patna College, Moradpore, P.O., Bankipore; M. R. Viswanatha Tyer, 50, Prem Chand Bural Street, Bow-Bazar, Calcutta.

The President announced that, at the request of the International Committee on Physico-Chemical Nomenclature, the Council invited criticism of the symbols recently suggested by the International Association of Chemical Societies. For these symbols Fellows were referred to the *Proc. Chem. Soc.*, xxix., 333 (see also Chem. News, cviii., 293), and were requested to forward any suggestions to Prof. A. Findlay, University College, Aberystwyth, before February 28, 1914.

The announcement was also made that, in order to give Fellows more frequent opportunity of meeting informally, the Rooms of the Society would be opened on January 15, 1914, at 8 p.m., when the President and Council would be glad to meet the Fellows of the Society. Smoking will be permitted, and light refreshments will be provided. Fellows were also invited to exhibit apparatus or specimens of interest and to show experiments; those willing to do so were requested to communicate with the Secretaries before the Monday previous to the Meeting.

Of the following papers, those marked * were read:—

*330. "*Absorption of Gases by Celluloid.*" By Victor Lefebure.

An absorption of gases by celluloids of a magnitude comparable with the sorption of gases by some charcoals has been observed by the author, and the chief points already established are as follows.

The effect is reversible. It is not chemical, in that no compound with a very low or with a moderately large dissociation pressure is formed, assuming that such compounds would not form solid solutions with the celluloid. It is common to all the kinds of celluloid examined, but almost vanishes when a precipitate of celluloid constituents is substituted for film celluloid. The property is recovered by the refilmed precipitate. Again, it is not exhibited by the two chief constituents of the celluloid, camphor and nitrocellulose. Finally, the effect increases with lowering of temperature and raising of pressure, and in general nature resembles a case of sorption.

The quantitative experiments which have been carried out are concerned with time, diffusion, and equilibrium. The equilibrium experiments yield isotherms of the type given by previously examined sorption effects. The time experiments, yielding curves representing rates of sorption, indicate the possibility of a development of surface within the celluloid mass, and probably near to the external visible surface. The diffusion experiments have merely established the fact of diffusion through films.

DISCUSSION.

Prof. DONNAN wished to congratulate the author on the excellent way he had carried out the work. He thought that Mr. Lefebure's paper was the first investigation of that nature on a semi-solid colloidal film.

The great rapidity of the initial absorption of the carbon dioxide by the celluloid, and the fact that the speed of absorption increased much more rapidly (per unit of weight of celluloid) than the increase of apparent (external) surface of the film, showed that in the mass of the celluloid or perhaps in the neighbourhood of the surface there was a very fine-grained macro-porosity into which the gas could rapidly penetrate and be adsorbed. Diffusion of the gas into or through molecular pores was simply what one called solution, and, so far as one knew, solution phenomena in semi-solid gels were relatively slow at the temperatures at which Mr. Lefebure had worked.

Solution and diffusion in the ordinary sense probably also occurred in the case of the celluloid films, and accounted for the later portions of the velocity curves.

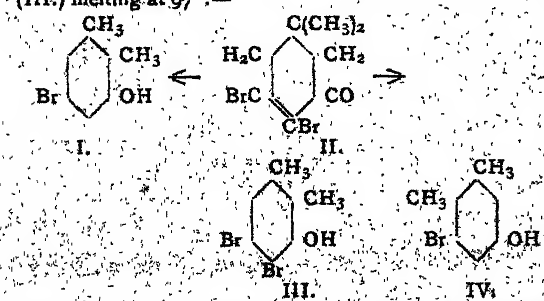
Very little was known concerning the macro-heterogeneity of the camphor-nitrocellulose system, but Mr. Lefebure's work was an important contribution to the subject.

Mr. W. P. DREAPER pointed out that it was possible to vary the porosity of structureless cellulose filaments within wide limits by varying the strain under which they were dried at the time of manufacture. It might be possible to utilise this in determining the effect of porosity on the adsorption of gases by this material, and in this way confirm, or otherwise, some of the conclusions arrived at by the author. From this point of view it was strange that the precipitated cellulose gave a lower result, as it would certainly expose a considerable surface to the gas, and be relatively porous.

*331. "*Aromatic Compounds obtained from the Hydroaromatic Series.* Part III. *Bromoxylenols from Dimethyldihydroresorcin.*" By ARTHUR WILLIAM CROSSLEY and NORA RENOUF.

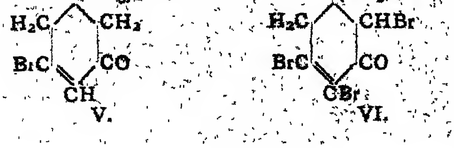
In continuation of the work, of which a preliminary note has appeared (*Proc.*, 1912, xxviii., 332), the following rearrangements of hydroaromatic to aromatic substances have been established:—

1. Under the influence of alcoholic potassium hydroxide dibromodimethyl*cyclo*hexenone (II.) gives 5-bromo-*o*-3-xylenol (I.) melting at 84° and 4:5-dibromo-*o*-3-xylenol (III.) melting at 97°:—



2. Heat causes the elimination of hydrogen bromide from dibromodimethyl*cyclo*hexenone, with production of 5-bromo-*o*-3-xylenol and 6-bromo-*o*-4-xylenol (IV.) melting at 103°.

3. Bromine acts on bromodimethyl*cyclo*hexenone (V.) to yield, in the first place, a mixture of hydroaromatic substances, which on heating loses hydrogen bromide to give 5-bromo-*o*-3-xylenol and 6-bromo-*o*-4-xylenol:—



4. Tribromodimethyl*cyclo*hexenone (VI.) under the influence of heat or alcoholic potassium hydroxide yields 4:5-dibromo-*o*-3-xylenol and other bromoxylenols, which, up to the present, it has not been found possible to separate in a pure state.

*332. "*The Equilibrium of Dilute Hydrochloric Acid and Gelatin.*" By HENRY RICHARDSON PROCTER.

The author referred to a previous paper (*Koll. Chem. Beihefte*, 1911, ii., 243), in which it was shown that the swelling of gelatin in dilute acids, and the amount of acid absorbed, can be explained on the current hypothesis of chemical affinity and osmotic pressure. Precise mathematical expressions for these relations were now given, and it was shown that the two basic affinity-constants of gelatin being known, together with molecular weight, and a small correction for original alkalinity, its whole behaviour with regard to dilute acids can be prognosticated. The mathematical relations are quite general and applicable to other amphoteric proteins and other acids and their salts, and all the concentrations in the jelly were shown to be mathematical functions of the concentrations of the equilibrium acid only, and not dependent on the chemical character of the protein. Gelatin appears to be diacid as a base, with hydrolysis constants $K_1 = 0.0013$, $K_2 = 1.05$, and an approximate molecular weight of 839, leading to the formula $C_{35}H_{57}O_{13}N_{11}$.

Some difficulties in the applications of the electrometric method to colloidal equilibria were mentioned, and it was pointed out that in consequence of surface-potentials the ionic concentrations measured with the concentration cell in colloid solutions are not those of the colloid solution itself, but of the acid or other solution with which it would be in equilibrium. Suggestions were made with regard to the probable colloidal structure of protein jellies and solution. A graphic geometrical method was described for dealing with all such equilibria as depend on the "equality of products."

DISCUSSION.

Prof. DONNAN thought that the methods of investigation employed by Prof. Proctor were the right ones, and would lead him eventually to a solution of his problems.

He observed that the author inclined to the view taken by Arrhenius in his work on immunity, namely, to treat the phenomena as cases of molecular equilibrium, without much reference to adsorption and colloidal aggregation and disaggregation.

Nevertheless in his (Prof. Donnan's) opinion both series of phenomena occurred, and must be taken into account.

He would refer Prof. Proctor to the work of two Italian investigators, an account of which was to be found in the "Nernst Festschrift."

*333. "*Researches on Residual Affinity and Co-ordination.* Part I. *Metallic Acetylacetones and their Absorption Spectra.*" By GILBERT T. MORGAN and HENRY WEBSTER MOSS.

An examination of the absorption spectra of fourteen metallic acetylacetones in alcoholic solution showed that, with the exception of the chromium compound, all these substances exhibit a well-marked absorption band in the ultra-violet.

Chromic acetylacetone showed a band of this character, but in addition a well-defined band toward the red end, probably due to the metallic radicle. Comparative experiments were made on the volatility of scandium and thorium acetylacetones under the ordinary and under 8—10 mm. pressure.

*334. "*Ionisation and the Law of Mass Action.* Part II. *The Osmotic Data in Relation to Combined Water.*" By WILLIAM ROBERT BOUSFIELD.

It was shown by reference to the figures for sucrose that the osmotic data can be brought into accurate conformity with the gas equation by taking account of the combined water. The osmotic-pressure equation, vapour-pressure equation, and freezing-point equations then present themselves in the following forms:—

O.P. equation $P/R'\theta\ (h-n)=i$
V.P. „ $\rho\ \delta p/p\ (h-n)=i$
F.P. „ $\Delta/F'\ (h-n)=i$,

where h is the total number of molecules of water per mol. of solute and n is the number of combined molecules of water per mol. of solute.

DISCUSSION.

Prof. DONNAN thought that there were some misconceptions in that paper. There was absolutely no *a priori* reason to "expect" the equation PV = RT to hold for more concentrated solutions.

The general theoretical osmotic equation for solutions of any strength was now well known. If, however, there was practically no volume or energy-change on solution, this equation, as was well known, reduced to a simple form for solutions of any concentration. If solvation occurred, then, of course, in relatively concentrated solutions allowance had to be made for it.

The calculations of Mr. Bousfield might serve to show that after this allowance had been made aqueous solutions of sucrose of very considerable concentration approximated to the "simple" behaviour referred to above. In Prof. Donnan's opinion this suggestion had been made by previous authors.

335. "*Chemical Examination of Sarsaparilla Root.*" By FREDERICK BELDING POWER and ARTHUR HENRY SALWAY.

The material used for the present investigation consisted of grey Jamaica sarsaparilla root, such as is recognised by the British Pharmacopœia.

The root was found to contain a small amount of an enzyme, which slowly hydrolysed amygdalin.

An alcoholic extract of the root yielded, besides a little essential oil, the following definite compounds:—(i.) a crystalline glucoside, sarsasaponin, $C_{44}H_{76}O_{20},7H_2O$, which, on hydrolysis, is resolved into sarsasapogenin, $C_{26}H_{42}O_3$, and dextrose; (ii.) sitosterol-*d*-glucoside (phytosterolin), $C_{33}H_{56}O_6$; (iii.) sitosterol, $C_{27}H_{46}O$; (iv.) stigmasterol, $C_{30}H_{50}O$; (v.) a new crystalline dicarboxylic acid, *sarsapic acid*, $C_6H_4O_6$ (m. p. 305°), which yields a *dimethyl* ester, $C_8H_8O_6$, melting at 121°; (vi.) dextrose; (vii.) a mixture of fatty acids, consisting of palmitic, stearic, behenic, oleic, and linolic acids. The alcoholic extract contained, furthermore, a small quantity of a substance which possessed the characters of cetyl-*d*-glucoside, and a considerable quantity of potassium nitrate was also present. The amount of resinous material was equivalent to about 1·25 per cent of the weight of root employed.

It has now been shown that Jamaica sarsaparilla root contains but one definite saponin glucoside, namely, sarsasaponin, and it is considered probable that the "parillin" of previous investigators was a mixture of sarsasaponin and a phytosterolin. It has also been definitely ascertained that the so-called "smilacin" ("smilasaponin" of v. Schulz) is not a homogeneous substance, but contains a relatively small proportion of sarsasaponin, together with amorphous material.

336. "*Metallic Derivatives of Acetylacetone and Acetyl Mesityl Oxide.*" (Preliminary Note.) By GILBERT THOMAS MORGAN and HENRY WEBSTER MOSS.

Series 1.—With the exception of copper, the metals of the first vertical series of the periodic classification yield somewhat unstable derivatives with acetylacetone. *Lithium acetylacetone*,—

$$Li\left[<\begin{matrix}O{:}C(CH_3)\\O{\cdot}C(CH_3)\end{matrix}\geqq CH\right],$$

a colourless, crystalline mass, decomposed when dissolved in the ordinary organic media, the solutions assuming a yellow colour.

Caesium acetylacetone, a colourless, crystalline mass soluble in water or alcohol, was much less stable than the preceding compound. Silver acetylacetone, obtained as a white, crystalline precipitate, rapidly darkened on exposure, with liberation of silver; it is sparingly soluble in water; the solution rapidly deposited a silver mirror. The blue copper acetylacetone yielded a green additive compound with quinoline.

Series 2.—Zinc acetylacetone, formerly described as a yellow substance, was obtained in colourless, acicular prisms, soluble in hot water or alcohol. Its cadmium analogue was much less soluble.

Series 3.—*Scandium acetylacetone*,—

$$Sc\left[<\begin{matrix}O{:}C(CH_3)\\O{\cdot}C(CH_3)\end{matrix}\geqq CH\right]_3,$$

melting after sublimation at 187—187·5°, crystallised from benzene in colourless, tabular prisms, or from chloroform in square plates. It was prepared by the interaction of scandium nitrate, acetylacetone, and ammonia. The molecular weight determined by the ebullioscopic method corresponded with the above formula.

Comparative experiments made with yttrium, erbium, and thorium indicate that the acetylacetones of scandium and yttrium (the two rare earth metals of least atomic weight) do not under similar experimental conditions yield additive ammonia compounds comparable with those obtained from acetylacetones of the rare earth metals of higher atomic weight.

Series 5.—*Vanadyl acetyl mesityl oxide*,—

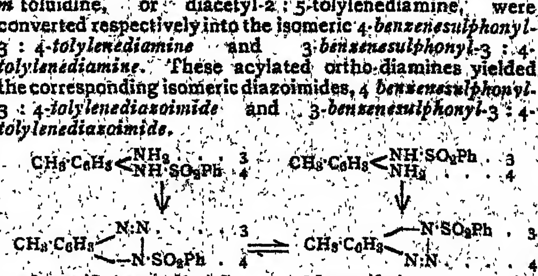
$$VO\left[<\begin{matrix}O{\cdot}C(C_4H_7)\\O{-}C(CH_3)\end{matrix}\geqq CH\right]_2,$$

prepared by the interaction of vanadyl sulphate, acetyl mesityl oxide, and ammonia, crystallised from light petroleum in grass-green leaflets.

Other metallic derivatives of acetyl mesityl oxide are under examination; they are characterised by their ready solubility in organic solvents, including light petroleum.

337. "*Constitution of the Ortho-diazoimines.* Part IV. *Isomeric Benzenesulphonyl*-3 : 4-*tolylenediazoimides.*" By GILBERT THOMAS MORGAN and GODFREY EDWARD SCHARFF.

3-Nitro-*p*-toluidine and 4-nitro-*m*-toluidine (m. p. 111—112°), the latter base prepared from either *m*-cresol, *m* toluidine, or diacetyl-2 : 5-tolylenediamine, were converted respectively into the isomeric 4-*benzenesulphonyl*-3 : 4-*tolylenediamine* and 3-*benzenesulphonyl*-3 : 4-*tolylenediamine*. These acylated ortho-diamines yielded the corresponding isomeric diazoimides, 4-*benzenesulphonyl*-3 : 4-*tolylenediazoimide* and 3-*benzenesulphonyl*-3 : 4-*tolylenediazoimide*.



α-Isomeride (m.p. 118—119°). β-Isomeride (m.p. 150—151°).

The α-isomeride is a more soluble, labile modification, which on prolonged boiling in solution changes almost completely into the less fusible, more sparingly soluble, stable β-isomeride.

338. "*Organic Derivatives of Silicon.* Part XXI. *The Condensation Products of Diphenylsilicanediol.*" By FREDERIC STANLEY KIPPING and ROBERT ROBISON.

The study of the four condensation products of diphenylsilicanediol previously described (Kipping, *Trans.*, 1912, ci., 2125) has been continued in order to ascertain the conditions under which each is formed.

The results seem to show that diphenylsilicone, $SiPh_2O$, the analogue of benzophenone, is not produced by the dehydration of diphenylsilicanediol, and that the closed-chain compound,—

$$SiPh_2<\begin{matrix}O\\O\end{matrix}>SiPh_2,$$

is not formed by the dehydration of anhydrobisdiphenlsilicanediol.

I the presence of piperidine, solutions of diphenyl-

silicanediol and of anhydrobisdiphenylsilicanediol both give tetra-anhydrotetrakisdiphenylsilicanediol, and probably also some trianhydrotrisdiphenylsilicanediol.

Dianhydrotrisdiphenylsilicanediol may be obtained by carefully hydrolysing trianhydrotrisdiphenylsilicanediol with alkali in ethereal acetone solution; it is very rapidly converted into trianhydrotrisdiphenylsilicanediol in methyl-alcoholic solution in the presence of a little hydrochloric acid. Trianhydrotrisdiphenylsilicanediol is also formed when anhydrobisdiphenylsilicanediol is treated with a methyl-alcoholic solution of hydrochloric acid, but the reaction takes place slowly.

Trianhydrotetakisdiphenylsilicanediol,—

$$HO{\cdot}SiPh_2{\cdot}O{\cdot}SiPh_2{\cdot}O{\cdot}SiPh_2{\cdot}O{\cdot}SiPh_2{\cdot}OH,$$

the most complex open-chain condensation product so far obtained, may be prepared by very cautiously hydrolysing the tetra-anhydro-derivative with sodium hydroxide in chloroform solution; it melts at 127°, and is easily converted into the tetra-anhydro-derivative by traces of sodium hydroxide in alcoholic solution.

339. "*The Absorption Spectra of Sulphurous Acids and Sulphites.*" (Preliminary Note.) By ROBERT WRIGHT.

While comparing the absorption spectra of various acids with their salts, it was found that whilst the absorption of sulphurous acid is characterised by a band in the ultra-violet, the sodium salt exhibits only general absorption. It is thought that this is most probably due to a difference in structure between the acid and its salt, additional evidence in favour of this view being the fact that whilst the acid has the properties of a moderately strong acid, its salt suffers hydrolysis in aqueous solution, thus behaving like a derivative of a weak acid.

A parallel case is to be found in the behaviour of chromic acid and its salts, where a strong acid differs in visible colour from its salts, the latter also being hydrolysable.

(To be continued).

NOTICES OF BOOKS.

Researches in Magneto-optics. By P. ZEEMAN, Sc.D., Ph.D., D.Sc. London: Macmillan and Co., Ltd. 1913.

THIS monograph contains a very stimulating account of the author's remarkable work in magneto-optics, and since highly technical details are omitted as far as possible it may be read by the educated general public with as much interest as by the scientific man. The author's manuscript has been translated from the Dutch by Miss J. D. van der Waals. The arrangement of the text closely follows the historical development of the subject, and the author's first paper on "The Influence of Magnetism on the Nature of the Light Emitted by a Substance," laid before the Academy of Sciences at Amsterdam in 1896, is reprinted almost in full. The apparatus employed in modern spectroscopic work is admirably described, and the investigations of other workers in the same sphere are fully described. Some new results are published in the monograph for the first time; for example, the determination of the ratio of the number of emitting atoms to the whole number present in the flame, and in the last chaper some account is given of Sir J. J. Thomson's work on the constitution of the atom.

General Chemistry Laboratory Manual. By J. C. BLAKE, Ph.D. New York: The Macmillan Co. 1913.

THIS book of practical chemistry is intended to be used as a laboratory companion to the author's "General Chemistry, Theoretical and Applied," and the numbering of the chapters and sections is the same as in the text-book. Methods of preparing many elements and inorganic compounds are described, and a short course of analytical work is included, besides a rather sketchy outline of practical work in applied chemistry, including very simple experiments with fuels, soils, waters, &c. The book will no doubt be found convenient by those who are using the text-book or attending the author's lectures at the Agricultural and Mechanical College of Texas, but it hardly presents sufficient novelty or special merit to suggest that its more extended use could be warmly recommended.

Calico Engraving. By WILLIAM BLACKWOOD. London: Charles Griffin and Co., Ltd. 1913.

THIS book is based upon the lectures delivered by the author at the Royal Technical College, Glasgow, on engraving designs for calico, but in preparation for the press the lectures have been very much extended, and both skilled designers and students will find the book most instructive. The author enters fully into technicalities, and machinery of many different types is thoroughly explained and illustrated. Valuable hints are given for the benefit of hand engravers, and engraving for paper stainers is also discussed. Electroplating is very briefly treated, and if the theoretical explanations are somewhat curtailed it is quite possible that they are sufficient for the purpose for which they are intended.

Practical Chemistry. By the late J. CAMPBELL BROWN, D.Sc., LL.D. Sixth Edition. Edited by GUY D. BENGOUGH, M.A., D.Sc. London: J. and A. Churchill. 1913.

THIS very useful book contains a concise summary of the chief reactions employed in analytical work, and includes a good deal of matter not usually to be found in similar books of the same size. Thus the reactions of some of the rarer elements are given, also those of many organic bases and of some neutral organic substances which are commonly used in the laboratory. The analysis of gases is also shortly treated. A great deal of information is compressed into the book, but for the use of students the directions may very possibly be found to be somewhat too concise. For example, unless used to gas analysis the student might be somewhat at a loss when told merely to "separate the gases into two groups by a solution of sodium hydrate." For practising analytical chemists, however, the book can be recommended as containing clear and accurate descriptions of experimental work.

Chemistry, Inorganic and Organic. With Experiments. By CHARLES LOUDON BLOXAM. Tenth Edition. Re-written and Revised by ARTHUR G. BLOXAM, F.I.C., and S. JUDD LEWIS, D.Sc., F.I.C. London: J. and A. Churchill. 1913.

FOR nearly fifty years Bloxam's "Chemistry" has enjoyed the well deserved reputation of being the most compendious work on chemistry in a single volume, and those who have had occasion to use it will probably not need to be reminded how often they have found in it information not to be obtained even from larger and more detailed treatises. The original author showed remarkable skill in selecting his material, and this feature is as noticeable in the last as in the first edition. Very many changes have had to be made in the tenth edition. Thus all the earlier chapters have been recast, and throughout the book the Periodic System of classification has been followed more closely than before. The division of the text into numbered paragraphs has been dropped, and the appendix on applied chemistry is omitted.

The Sugars and their Simple Derivatives. By JOHN E. MACKENZIE, D.Sc., Ph.D. London: Gurney and Jackson. 1913.

THIS book is based upon a course of lectures delivered by the author at Birkbeck College, London, and afterwards at the University of Edinburgh. Many students who were interested in technological chemistry attended these lectures, and for their benefit stress was laid upon those

points in the chemistry of the sugars which are of special importance in the sugar and brewing industries and in medicine. At the same time the book gives a really useful introduction to the subject for students of pure chemistry, and questions of configuration, &c., are so clearly treated that candidates for examinations will find it a valuable summary. The first part of the book contains some account of the production and manufacture of cane-sugar, and subsequently the properties and constitution of the individual sugars are described. Fermentation and metabolism are shortly dealt with in later chapters.

Principles and Processes of Metal Plate Work. By Edwin G. Barrett. London: Crosby Lockwood and Son. 1914.

This book has been compiled to meet the requirements of candidates for the examination in metal plate work of the City and Guilds of London Institute, and it will be found to fulfil its purpose admirably. The author has carefully studied the examiners' criticisms of the average candidate's work, and has paid special attention to those points in which particular weakness is usually displayed. Thus methods of performing numerical calculations are very carefully explained, and many mensuration formulæ are given. Model answers are also provided, and the syllabus of the examination in metal plate work and also recent questions are reproduced. The book will be of service to metal plate workers other than those entering for the examination, and if they wish to acquire some knowledge of the theory of such work they cannot do better than to get a copy of it.

The London Matriculation Directory. No. 65, September, 1913. London: University Tutorial Press, Ltd.

No. 65 of the "Matriculation Directories" closely resembles its predecessors, and contains the usual articles on text-books, details of the classes of the University Correspondence College, and hints to intending candidates for the examination. Many of the papers sent in September, 1913, are reproduced in it with full solutions and comments upon them. Although on the whole a wise choice is made of the papers for reproduction, and they deal with those subjects which are most popular in the examination, it seems probable that some students would be glad to see some of the others, such as those on Ancient History, Geology, or Zoology, even if it were not worth while to prepare answers to them.

London University Guide, 1914. London: University Correspondence College.

This guide contains a full almanac and calendar for 1914, with the regulations of the more important examinations. Details of the classes and the fees of the University Correspondence College are also given, and the guide contains some articles on text-books and an interesting short history of the University of London and account of its constitution. Recent changes in the regulations are pointed out, and the guide is an almost indispensable possession for the intending candidate for an examination of London University.

The Burroughs Wellcome Photographic Exposure Record and Diary for 1914.

Contains much useful information for photographers. The "Record of Negative Exposures" is invaluable for any who care to introduce "method" into their work, and the Exposure Calculator is an ingeniously designed apparatus by help of which the correct exposure can be calculated. Some very good prints are included in the book; one of Mr. H. C. Ponting, F.R.G.S., at work in his dark room at Cape Evans, speaks well for the value of the comparatively new developer Rytol. There is a good diary and memorandum book included, and the book is not too bulky for the pocket or the camera case.

CORRESPONDENCE.

SPECIFIC GRAVITY DIFFERENCES.

To the Editor of the Chemical News.

Sir,—It is a curious fact, which I have never seen noted elsewhere, that if the six cases which I can readily call to mind and find figures for in which there are three varieties of a substance, in four cases the difference in the specific gravity between the first two is equal to the difference between the second two:—

1.	Diamond	3·514	
			1·01
	Graphite	2·5	
			1·05
	Amorphous carbon	1·45	
2.	Grey arsenic	5·527	
			1·0
	Black arsenic	4·7	
			1·0
	Yellow arsenic	3·7	
3.	Rhombic tin	7·25	
			0·70
	Tetragonal tin	6·55	
			0·75
	Grey tin	5·8	
4.	Aragonite	2·93	
			0·21
	Calcite	2·72	
			0·20
	Vaterite	2·52	

It is hard to see that there can be any significance attached to this, but the mathematical odds against it being entirely due to chance are very great. Moreover, in the case of one of the exceptions, silica, the second difference is almost an exact multiple of the first.

Quartz	2·67	
		0·34 (= 3 × 0·11)
Tridymite	2·33	
		0·11
Vitreous	2·22	

In the last case, that of sulphur, no such relation is evident, the difference between rhombic and monoclinic sulphur being 0·13, and that between monoclinic and amorphous sulphur 0·02.—I am, &c.,

Edgar B. Wastell.

31, Gillott Road, Birmingham.

INSTITUTE OF CHEMISTRY CONFERENCE.

To the Editor of the Chemical News.

Sir,—With your permission I should like to reply to the letter of Mr. E. A. Lewis, which was published in your issue of the 2nd January.

The last part of his letter raises an important point of general interest.

It is essential that the chemical profession should include all persons who are engaged in teaching the principles of chemistry, or in applying those principles towards the attainment of practical results. These persons only can claim to be professional men in the sense in which that term is usually accepted. The profession should not include those persons whose interests are directly commercial.

Any profession worthy of the name should consist of a united body of men, but true professional unity is not attained by setting up, at the outset, educational barriers of a more or less artificial kind.

This mistake, however, has been made in the case of the chemical profession, with the result that the profession has been divided against itself, the status of technical chemists has been lowered, their professional interests endangered, and the technical interests for which the profession stands have suffered.

It is unnecessary to insist on the national importance of applied chemistry. The fact that universities and technical colleges give a large amount of time and money in training students in the principles of chemistry is sufficient proof of this.

Students are encouraged to pursue a course of study that shall form a sound foundation for their future technical work. They are encouraged to adopt applied

chemistry as a calling, but no appeal is made to them on the grounds that it is a profession.

The neglect of this cardinal fact has led to the present deplorable state of things.

It is the first duty of a chemical professional body to encourage the development of a professional spirit—which at present is almost entirely wanting—and to include in the profession all those who are actively and personally engaged in applied chemistry.

As your correspondent points out, there are many men, with perhaps slender academic qualifications, whose technical qualifications fully entitle them to speak with authority.

It may be added that there are an even larger number of younger men who have not had either time or opportunity to prepare for purely educational tests and whose technical experience is naturally inconsiderable.

To deny by implication that both these types of men have no professional status is an absurdity and worse than an absurdity.

A professional organisation is needed that has broad and sympathetic views and the will to follow and enforce a strong policy in order that the chemical profession may ultimately rank equally with other great professions, and that its members may, without distinction, obtain the status to which their services entitle them.—I am, &c.,

J. Wilberforce Green, Secretary,
The Association of Chemical Technologists.

30, Victoria Street, Westminster, S.W.,
Jan. 21, 1914.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clvii., No. 23, December 8, 1913.

Transformation of Essence of Citron into Essence of Roses.—Ph. Barbier and R. Locquin.—The authors have found that by the action of various reagents, such as the hydracids, for example, it is easy to transform citronellol into rhodinol, but the reverse change cannot be effected. This explains why commercial citronellols frequently smell of rhodinol, and also why, starting from either *d*-citronellol or *l*-rhodinol, various authors have obtained the same derivatives. Thus the three rhodinols foretold by theory are actually known, viz. :—(i.) The *l*-rhodinol of essence of roses or of pelargonium ; (ii.) the *d*-rhodinol which is obtained by the tranposition of *d*-citronellol or indirectly from natural *d*-citronellol; (iii.) the *i*-rhodinol prepared by MM. Bouveault and Gourmand by the reduction of synthetic ethyl rhodinate.

Neutralisation of Periodic Acid.—René Dubrisay.—By the method of capillary volumetry which he has previously described the author has proved that periodic acid is tribasic. In order to demonstrate the third basicity it is necessary to work with very dilute solutions, and it appears that the capillary method is more sensitive than the method of electric conductivity for the study of neutralisation. The third basicity of both phosphoric and periodic acids is detected thus, while conductivity determinations do not reveal it.

Action of Carbon Oxychloride on Phosphates and Silicates.—J. Barlot and Ed. Chauvenet.—When phosphates are exposed to the action of $COCl_2$ at temperatures of from 350° upwards the following reaction occurs: $P_2O_5.3MO + 6COCl_2 = 2POCl_3 + 6CO_2 + 3MCl_2$. With silicates the reaction is $SiO_3M + COCl_2 = SiO_2 + CO_2 + MCl_2$. Thus phosgene gas is a very suitable reagent for attacking phosphates and silicates in order to analyse them, or for preparing anhydrous metallic chlorides from these minerals. Whatever the state of combination of the metal (oxide, sulphide, nitrate, carbonate, sulphate), it is readily transformed into anhydrous chloride.

Nitration of Paraiodoacetanilide.—E. Jungfleisch.—By varying the experimental conditions the nitration of paraiodoacetanilide can be made to yield either the isomer $C_6H_4I^4(NH_2)^1$, or a mixture of products including the acetyl derivative of pa anitroaniline, diiodo-acetanilide, the acetyl derivative $C_6H_3I^4(NO_2)^2(NHCOCH_3)^1$, and a substance which appears to be the acetyl derivative of an iodonitraniline.

Bulletin de la Société Chimique de France, Vol. xiii.-xiv., No. 20—21, 1913.

New Preparation of Epichlorhydrine.—Jean Nivière.—Epichlorhydrine can be prepared by the action of quicklime on symmetrical dichlorhydrine. The lime is placed in a flask which is heated on a water-bath, the pressure being reduced to 120 mm. The dichlorhydrine is allowed to fall in drop by drop, and epichlorhydrine then distils over. The yields are very satisfactory, 93 to 95 per cent of the theoretical amount of pure epichlorhydrine being obtained, boiling at 116—119°, after drying over K_2CO_3.

Action of Dimethylamine upon the Iodohydrines Derived from Styrolene. Study of the Two Phenyl-dimethylamino-ethanols.—M. Tiffeneau and E. Fourneau.—The authors have prepared two isomeric iodohydrines from styrolene; the one, $C_6H_5.CHOH.CH_2I$, is obtained by the action of iodine and mercuric oxide on styrolene in solution in aqueous ether, while the other, $C_6H_5.CHI.CH_2OH$, which is crystalline, is formed by the fixation of HI on styrolene oxide. When these two compounds react with dimethylamine in the cold they yield the same amino-alcohol. This amino-alcohol is different from that which would normally be obtained with the crystallised iodohydrine, if the intermediate formation of oxide of styrolene, $C_6H_5.CHN(CH_3)_2.CH_2OH$, did not occur. This amino-alcohol can be prepared from the corresponding etherified acid, $C_6H_5.CHN(CH_3)_2.CO_2C_2H_5$, by reduction by Blanc and Bouveault's method. This latter amino-alcohol is quite different from that furnished by the iodohydrines. Thus it has been proved, as far as the halogen hydrines are concerned, that the intermediate formation of oxide of ethylene occurs, so that ammonia and the primary and secondary amines cannot be used to determine the structure of the halogen hydrines. The authors have prepared many derivative of the two amino-alcohols.

Constitution of Trinitro-*p*-aminophenols and of Trinitro-*p*-anisidines.—Frédéric Reverdin and Raphael Meldola.—Two isomeric trinitro-*p*-anisidines are known of m. p. 127—128° and 138—139° respectively. One of their nitro-groups is extremely mobile, and many syntheses have been effected owing to this property. The authors have arrived at the general conclusion that in the latter it is always the nitro-group at 3 which is mobile, while in the isomer of melting-point 127° it is the group at 2 which is mobile under the influence of basic reagents, while the 3-group is mobile after diazotation under the influence of the neighbouring diazo-group. They have also proved that the original trinitroacetylaminophenol, from which the anisidines were derived, was not the 2.3.5- but the 2.3.6-compound.

Soluble Caseins in Milk.—L. Lindet.—The author has confirmed his previous results relating to the presence of two soluble albuminoids in milk, and has further shown that the sum of these two caseins is practically constant, although the proportion of each of them is very variable. They adhere by capillarity to the casein in suspension.

Determination of very Small Quantities of Chlorides in Waters.—Maurice Lombard.—150—200 cc. of water are boiled until all the calcium bicarbonate is decomposed; the water is allowed to cool, it is brought up to its original

volume, and 100 cc. of the clear liquid are poured off. Then 5 drops of a 10 per cent solution of potassium chromate are added, and the same quantity to 100 cc. of distilled water containing, say, 5 mgrms. of NaCl per litre. Standard silver nitrate solution is then added to the known solution till a sufficiently distinct coloration is obtained, and then the silver nitrate is added to the water under examination until precisely the same tint is obtained. The calculation is very simple. If, for example, 1·8 cc. was added to the known solution (100 cc. of NaCl containing 5 mgrms. per litre) and 2·65 to the unknown solution, then 2·65—1·8 or 0·85 cc. correspond to 0·497 mgrm. of NaCl, which added to the 0·5 mgrm. in the comparison solution gives 1 mgrm. of sodium chloride in 100 cc., or 10 mgrms. per litre. The method is very sensitive, and quantities of chloride which are less than 0·5 mgrm. per litre can be determined by it.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xlvi., No. 14, 1913.

Organic Silicon Compounds from Silicon Hexachloride and Methyl Magnesium Bromide or Iodide.—Geoffrey Martin.—The author has already described the formation of a substance, approximately of the composition $CH_3.Si_6O_{13}H_9$, which, when dissolved in caustic potash, liberates about 169 cc. of hydrogen per grm. By varying the experimental conditions compounds containing more methyl groups can be obtained, *e.g.*, $(CH_3)_2Si_6O_{12}H_6$, $(CH_3)_4Si_6O_{12}H_2$, $(CH_3)_5Si_6O_{11}H$, and $(CH_3)_8Si_6O_7H_2$. The quantity of hydrogen generated is less the greater the number of methyl groups present in the molecule. In the course of these experiments the author has prepared Bygden's hexamethyl-silicoethane, $Si_2(CH_3)_6$, and investigated its chemical properties. This substance does not liberate hydrogen on treatment with caustic potash, although it contains the Si—Si group.

Manganese Carbides and their Preparation by Heating the Metal in a Current of Methane.—Siegfried Hilpert and J. Paunescu.—When finely powdered manganese is treated with methane or methane and hydrogen at temperatures from 600—900° carbides result. With pure methane carbides containing up to 20 per cent C can be obtained, and with mixtures of equal volumes of methane and hydrogen carbides containing 15 per cent C. The saturation limits established for different temperatures do not correspond to simple atomic proportions. From their behaviour towards acids it may be deduced that the carbides are not derivatives of simple hydrocarbons, like calcium and aluminium carbides. Carbides containing up to 7 per cent C are ferromagnetic.

Modifications of Phosphorus.—Alfred Stock and Erich Stamm.—Smits and Leeuw have stated that different modifications of phosphorus exist in the melt of colourless phosphorus, and that the ordinary melting-point of colourless phosphorus (44·1°) is raised several degrees if the substance is first heated to 100° and then rapidly cooled. The authors cannot confirm these results. From the study of the melting- and solidification-points of red phosphorus it is observed that the melts behave like solutions and not like simple substances. The vapour arising from red phosphorus consists chiefly of P_4. From superheated phosphorus vapour more red phosphorus is deposited than was dissociated, so that obviously P_4 molecules take part in the formation of molecules of red phosphorus.

MISCELLANEOUS.

Royal Institution.—On Thursday next, February 5, at 3 o'clock, Prof. Sir Thomas H. Holland begins a course of two lectures on "Types and Causes of Earth Crust Folds." The Friday Evening Discourse on February 6 will be delivered by Dr. H. S. Hele-Shaw on "The Mechanics of Muscular Effort"; and on February 13, by Prof. J. Norman Collie, on "Production of Neon and Helium by Electric Discharge."

Economical and Accurate Testing of Mixtures without Weighing.—Manufacturers are often impressed with the time occupied in weighing the different ingredients required in the constitution of their several articles of manufacture; and, what is of still more importance, the accuracy of the several weighings are liable to serious irregularities. These several obvious requirements have induced Messrs. W. and T. Avery, Ltd., of the Soho Foundry, Birmingham, to design and manufacture a machine which exactly meets the case. The machine is of simple yet solid design. The steelyard is graduated to meet the wishes of the manufacturer, and buckets are hung from each of the hooks. In this case a quantity of one ingredient is placed in the bucket on the left of the fulcrum, and the moving poise is placed on the 20 per cent graduation, and when the latter balances the steelyard the ingredients will be found to be in the proportion of 80 and 20. The steelyard can be marked in any desired manner to suit the requirements of any particular trade, effecting a great saving in time and ensuring absolute accuracy. This machine can also be arranged to weigh the total of the mixture.

MEETINGS FOR THE WEEK.

MONDAY, Feb. 2nd.—Royal Institution, 5. General Meeting.
— Society of Chemical Industry, 8. "Oxygen and Metallic Antimony in Crude Antimony," by W. R. Schoeller. "Estimation of Zinc in Coinage Bronzes by Volatilisation," by T. K. Rose. "Nickel Tannates," by P. Singh. Opportunity will be given for discussing the following Paper:—"The Electrical Conductivity of Milk during its Concentration, with suggestions for a Practical Method of Determining the End-point in the Manufacture of Sweetened Condensed Milk," by L. C. Jackson, L. McNab, and A. C. H. Rothera.
— Royal Society of Arts, 8. (Cantor Lecture). "The Relation of Industry to Art," by Sir Charles Waldstein, Litt.D., Ph.D.

TUESDAY, 3rd.—Royal Institution, 3. "Animals and Plants under Domestication," by Prof. W. Bateson, F.R.S., &c.
— Royal Society of Arts, 4.30. "The Montreal, Ottawa, and Georgian Bay Canal," by Sir Robert Perks, Bart.

WEDNESDAY 4th.—Society of Public Analysts, 8. (Annual General Meeting). "Iodometry of Arsenic, Copper, and Iron," by G. D. Lander and J. J. Geake. "Composition and Analysis of Compound Liquorice Powder," by A. E. Parkes and F. Major. "Composition of the Saline Matter adhering to certain Wet Salted Skins" by M. C. Lamb.
— Royal Society of Arts, 8. "Motor Fuels, with special reference to Alcohol," by William Ormandy, D.Sc., &c.

THURSDAY, 5th.—Royal Institution, 3. "Types and Causes of Earth Crust Folds," by Prof. Sir T. H. Holland, F.R.S.
— Royal Society. "Conduction of the Pulse Wave and the Measurement of Arterial Pressure," by L. Hill, J. McQueen, and M. Flack. "Report of the Monte Rosa Expedition of 1911," by J. Barcroft, M. Camis, C. G. Mathison, F. Roberts, and J. H. Ryffel. "Notes on Soil Protozoa," by C. H. Martin and K. Lewin. "Development of the Starfish *Asterias Rubens*, L.," by J. F. Gemmill. "Floral Mechanism of *Welwitschia Mirabilis* (Hook)," by A. H. Church.
— Chemical, 8.30. "Absorption Spectra of the Vapours and Solutions of various Substances containing Two Benzene Nuclei," by J. E. Purvis. "Oxidation of some Benzyl Compounds of Sulphur—Part II., Benzyltetrasulphoxide," by J. A. Smythe. "Reaction between Iodine and Aliphatic Aldehydes," by H. M. Dawson and J. Marshall. "Erosion of Lead," by J. F. Liverseege and A. W. Knapp. "Acylation as Influenced by Steric Hindrance—The Action of Acid Anhydrides upon 3:5-Dinitro-*p*-aminophenol," by R. Meldola and W. F. Hollely.

FRIDAY, 6th.—Royal Institution, 3. "The Mechanics of Muscular Effort," by H. S. Hele Shaw, F.R.S.

SATURDAY, 7th.—Royal Institution, 3. "Neglected Musical Composers," by Prof. F. Corder.

THE CHEMICAL NEWS.

VOL. CIX., No. 2828.

HISTORY OF THE DISCOVERY OF FORMIC ACID.

By F. D. CHATTAWAY.

BEFORE the beginning of the sixteenth century some naturalist had observed with surprise that the blue flowers of chicory became reddened when thrown upon an ant-hill. This fact is recorded by early writers on botany—thus Brunfels* in 1536 writing of chicory, which he calls "Solsequium, "Cichorium," or "Sponsa solis," says:—"Flos eius miectus formicarum cumulo in rubrum uertitur colorem, idque magno naturae miraculo," and Hieronymus Tragus† a little later, in 1552, makes a similar but more elaborate statement:—"Sed quod fere preterieram, nature miraculum in hoc quoque flore obseruare licet. Siquidem non tantum ad solis ortum et occasum sese pandit et recondit uerum etiam cumulo formicarum abditus caeruleum colorem in rubeum mutat, ac si terrore illarum erubesceret."

The observation evidently aroused interest, for it is quoted by later writers. Thus Langham,‡ in the "Garden of Health," writes in 1577:—"Cast the flowers of Cycory among a heap of Ants or Pismires and they will soone become as red as blood"; while Bauhinus,§ more than half a century later, repeats the statement of Brunfels:—"Flos Solsequii ut Brunfels annotat seu Cichorii, iniectus formicarum cumulo in rubrum vertitur colorem, idque magno naturae miraculo."

Our exact knowledge of formic acid, however, really begins with a letter of John Wray‖ published in the *Transactions of the Royal Society*¶ for 1670, in which he compiles from the statements of two friends, Dr. Hulse and Mr. Samuel Fisher, an account of an acid liquid obtained by distilling ants with water. Wray was apparently only interested in the matter as a curious phenomenon, and wrote the letter with a view to elicit further investigation. As was his wont he fully acknowledged the sources of his information, and says that what he sends "concerning the Juyce of Pismires" he received from Dr. Hulse and Mr. Samuel Fisher,** of Sheffield. The former having met with the passage quoted above from Langham had written to Wray, as follows, in a letter dated Aug. 10th, 1669:—"I presently got some Cichory flowers and made the Experiment, and find it to be true what he saith, only he takes no notice of the manner how the flowers come to be stained; which therefore take as follows: Bare an Ant-hill with a stick, and then cast the flowers upon it and you shall see the Ants creep very thick over them. Now as they creep they let fall a drop of liquor from them and where that chanceth to light there you shall have in a moment a large red stain. Sometimes they will be a pretty while before they discolour them and at other times they will do it suddenly. At first I guessed that being vext by stirring their hill they might thrust their stings into the flowers, and thorow them convey that sharp liquor. But by bruising them and rubbing the expressed juyce against the flowers I find they will be equally stained. 'Tis a thing well known that Ants, if they get into people's clothes and so to their skin, will cause a smart and tingling as if they were nettled; which I conceive is done by letting fall the fore-mentioned corrosive liquid rather than by stinging. To what sort of liquor to refer this Juyce I know not. . . ."

On reading this letter Wray called to mind an experiment which Mr. Samuel Fisher, of Sheffield, had made him acquainted with some years before, that "If with a staff or other instrument you stir an heap of Ants (especially Horse-Ants) so as to anger them they will let fall thereon a liquor which, if you presently smell to, will twinge the Nose like newly distilled Spirit of vitriol." He thereupon sent to enquire of Mr. Fisher what "Trials he had made of it," and received in reply the following account:—

"A weak Spirit of Pismires will turn Borage flowers red in an instant. Vinegar a little heated will do the like. Pismires distilled by themselves or with water yield a Spirit like Spirit of Vinegar, or rather like the Spirit of *Viridis aeris*. Lead put into this Spirit, or fair water, with the animals themselves being alive, maketh a good Saccharum Saturni . . . . when you put the Animals into water you must stir them to make them angry and then they will spirt out their acid juyce."

Fisher continues that he is not acquainted with any other animal that on distillation yields an *acid* spirit, and asks "whether any ingenious person conversant in these inquiries hath either himself found out or heard of any other animal that by distillation or otherwise yields an acid spirit."

Wray states that he has not, and adds*:—"Indeed, it seems strange that nature should prepare and separate in the Body of this Insect without any sensible heat and that in good quantity considering the bulk of the animal, a liquor the same for kind with those Acid Spirits which are by Art extracted out of some minerals not without great force of Fire." He concludes:—"I doubt not but this liquor may be of singular use in medicine. Mr. Fisher hath assured me that he himself hath made trial thereof in some diseases with very good success."

The acid liquid obtained from ants naturally attracted from time to time the attention of chemists, who at first concerned themselves with demonstrating the individuality of the acid and preparing its various salts. No considerable additions to the observations of Hulse and Fisher were, however, made till Margraf, about the middle of the eighteenth century, took up the study of the acid.

He writes†:—"During the months of May and June of this year (1749) I collected a quantity of these lively little

* Brunfels Otto (Brunfelsius Otho, "Herbarum vivae eicones . . . Argentorati apud Joannem Schottu, 1530-1531-1536," vol. iii., published 1536, p. 95). Mrs. Arber, to whose kindness I am indebted for these references, writes:—"Since Brunfels derives nearly all his text from previous writers, especially Dioscorides, I should expect that the statement about the ants and chicory did not originate with him. He says himself that his descriptions are 'extracted from ancient and trustworthy authors.'"

† "Hieronymi Tragi, de stirpium, maxime earum, quae in Germania nostra nascuntur," Lib. I., Cap. xci., page 271. (Argent., 1552, 4°).

‡ "The Garden of Health"; Conteyning the sundry rare and hidden virtues and properties of all kindes of simples and plants, together with the manner how they are to be used and applied in medicine for the health of man's body, against divers diseases and infirmities common amongst man. Gathered by the long experience and industry of William Langham, Practitioner in Phisicke. Imprinted at London, 1577. Page 144 at end of section on "Cicory."

§ Bauhinus, "Historiae plantarum universalis," Tom II., Lib. xxiv., page 1010. (Ebroduni, 1651).

‖ John Ray (1627-1705), the distinguished naturalist and botanist. In his letter to the Royal Society he spells his name Wray, but later in the same year dropped the initial W. He refers to the change in a letter to Dr. Lister, dated Aug 22nd, 1670, where he tells him that he reassumes the name of Ray, Wray being contrary to the way of his forefathers writing their names. He was, however, apparently also influenced by the circumstance that it was not possible to Latinise Wray. He used Wray all the time he was at Cambridge, his name being always thus spelt in the registers of Trinity College.

¶ *Phil. Trans.*, 1670, v., 2063. Extract of a letter written by Mr. John Wray to the publisher, dated Jan. 13, 1670, "Concerning some uncommon Observations and Experiments made with an acid Juyce to be found in Ants."

** Kopp, *Geschichte der Chemie*, iv., 362, refers incorrectly to Wray's Sheffield friend as "Samuel Fischer—a German," but states that he has not been able to get exact information on the point.

* It may here be noted that comparatively strong formic acid is ejected as a means of defence by various caterpillars. Will (*Jahresbericht*, 1847-1848, p. 546) has shewn that in caterpillars and especially in the Processionary caterpillar (*Bombyx processionea*) formic acid is present in the free concentrated condition, and Poulton (*Brit. Assoc. Rept.*, 1887, p. 765) has described how the larvae of the genus *Cerura* (*Dicranura*) have the power for purposes of defence of ejecting, when disturbed, a secretion containing about 40 per cent of formic acid. A larva which has not been irritated previously will eject 0·05 grm. of such a liquid.

† "Opuscules Chymiques," Paris, 1762, vol. i., page 294.

animals intending to extract not only the oil which they contain but also the acid. To this end I put them into an ample glass retort, poured in water, and placed it in a capsule of sand. Having adapted a suitable receiver and luted the joints I undertook the distillation, gradually increasing the heat until the water boiled. . . . I found in the receiver a water which was somewhat acid with the essential oil of ants floating on the surface. I separated this oil from the water as one ordinarily does it with some cotton, and preserved it in spirit."

The acid liquid he re-distilled and combined the distillate with the alkaline earths and the alkalis.* From an examination of the salts produced, Margraf concluded that the acid, while resembling in many respects the acid of vinegar, did not possess all the properties of the latter. The study of the acid was continued in a careful and systematic manner by Arvidson and Oehrn,† who described it and its salts with great exactitude. They supported Margraf's view that formic acid was not identical with the acid of vinegar by showing that if solutions of the two acids of the same specific gravity were prepared a given quantity of any base did not require the same amount of each for neutralisation. Deyeux‡ also about the same time expressed the opinion that formic acid was "un acide *sui generis*" though closely resembling acetic acid in properties.

Hermbstadt§ some few years later occupied himself specially with the purification of the acid, but came to the erroneous conclusion that malic acid was present in the expressed juice of ants.

Richter,‖ in 1793, showed how the acid might be concentrated by combining it with potash and distilling the dry salt with the exact amount of sulphuric acid, diluted with its own weight of water, required to neutralise the base used.

Some few years later, Fourcroy and Vauquelin advanced the statement, based on very superficial and insufficient work, that the acid obtained from ants was in reality a mixture of acetic and malic acids.¶

The contradictory statements which had been made up to this time respecting the acid induced Suersen** to submit it again to examination. In a dissertation published in 1805 he showed that the experiments of Fourcroy and Vauquelin did not justify their conclusions. He proved that formic acid suitably purified did not contain malic acid, and that it differed from acetic acid in several of its properties.

In 1812 Gehlen†† having prepared with great care formic and acetic acids and the copper and barium formates and acetates, compared their properties anew. He both criticised previous work, and pointed out with great clearness the peculiar characters of formic acid, and thus definitely established its individuality.

Berzelius‡‡ attempted in 1817, but with no great success, to determine the percentage composition of formic acid. This was first done in 1834 by Liebig, who employed his new method of elementary analysis.

In his famous essay upon manganese Scheele§§ records, in 1774, that when diluted vitriolic acid sugar and manganese are heated together "there arises a vapour that vellicates the nose, and if it be collected in a receiver appears to be pure vinegar." Westrumb later, in 1785, mentions that vinegar is produced by the dephlogistication of tartaric acid by means of oxide of manganese.

Döbereiner, in 1822, showed that the acid produced in this reaction is really formic acid. He says*:—"If tartar or tartaric acid and black oxide of manganese are placed in water and the mixture warmed, violent action ensues. The temperature rises, and a large quantity of carbonic acid gas is evolved. There distils over at the same time a clear liquid which superficially resembles acetic acid, but is shewn by a more exact examination to be formic acid." He discovered that the acid had the property of reducing the salts of the noble metals, and that it breaks up into water and carbonic oxide under the influence of sulphuric acid.

Döbereiner described later a method of preparing formic acid artificially in large quantity by the oxidation of sugar. He writes†:—"Should chemists and physicians make use of formic acid and its compounds they can be most advantageously obtained according to my experience by the partial oxidation of sugar," and then describes the process.

"A solution of 1 part of sugar in 2 parts of water is heated to 60° C. with $2\frac{1}{2}$ or 3 parts of finely powdered manganese dioxide in a copper still, which, as the liquid is very apt to froth up, must have at least fifteen times the bulk of the mixture; a third part of a mixture of 3 parts oil of vitriol, and 3 parts water is then gradually added, whereupon carbonic acid gas loaded with vapour of formic acid immediately escapes with violence. The head and condensing tube must now be quickly put on, and when the violent action has subsided the other two-thirds of the dilute sulphuric acid added, the mixture being stirred all the while, after which the liquid is gradually distilled almost to dryness. The distillate, which is transparent and colourless, is saturated with chalk, and the filtrate evaporated to the crystallising point, or if it be desired to obtain the acid the distillate is saturated with sodium carbonate, evaporated, and 7 parts of the dry residue distilled with a mixture of 70 parts oil of vitriol and 4 parts of water.

"This process is a very good one, 1 pound of sugar gives as much formic acid as will saturate 5 to 6 ounces of calcium carbonate, but the formic acid which it yields is slightly contaminated with acetic acid. To remove this impurity the distillate should be saturated while yet warm, not with sodium carbonate, but with carbonate of lead, and the solution evaporated to the crystallising point; the more soluble acetate of lead remains principally in the mother-liquor, and the formate of lead thus obtained must be distilled with a mixture of equal parts of oil of vitriol and water."

Wohler, later,‡ found it advantageous to use starch, and Liebig§ gives a method which differs little from Döbereiner's, except that starch is used in place of sugar.

In 1831, Pelouze‖ discovered that formic acid could be obtained from hydrocyanic acid and the cyanides. Anhydrous hydrocyanic acid was mixed with about its own volume of fuming hydrochloric acid. After four to five minutes the liquid solidified to a crystalline mass with sensible disengagement of heat. This was submitted to distillation, when it volatilised without residue, and gave successively hydrocyanic acid, hydrochloric acid, formic acid, and finally ammonium chloride. Pelouze also found that when a concentrated aqueous solution of potassium cyanide was boiled, out of contact with air, ammonia was liberated, and potassium formate produced. The hydrolysis of the cyanide at first took place rapidly, but as the action proceeded became slower and slower, and was not com-

* Thouvenal (1747-1815) used an ingenious method to obtain formates. He spread linen impregnated with potash on uncovered ant-hills, "the ants running over the cloth emitted their acids and odorant principle of the same nature which they exhaled in so great an abundance as to saturate the fixed alkali spread on the cloth. The lixivium of these linens afforded by evaporation a neutral salt crystallised in flat parallelograms and prismatic columns which were not deliquescent." Fourcroy's "Chemistry," London, 1788, vol. iv., p. 422.

† "Dissertatio chemica de acido formicarum," Upsala, 1777.

‡ *Journal de Physique*, 1778, xxii., 352.

§ "Physikalisch-chemische Versuche und Beobactungen, 1789, vol ii., pages 5—36.

‖ *Ueber die neuern Gegenstände der Chemie*, 1796, vi., 135.

¶ *Annales du Museum National d'Histoire Naturelle*, vol. i., page 333; *Gehlen's Journal der Chemie*, 1804, ii., 42. They afterwards admitted that they had mistaken phosphoric acid, which the juice of ants contains, for malic acid.

** *Gehlen's Journal der Chemie* 1805, iv., 3.

†† *Schweigger's Journ. Chem. u. Phys.*, 1812, iv., 1—41.

‡‡ *Annals of Philosophy*, ix., 107; *Ann. Chem. Phys.*, iv., 109.

§§ *K. Svenska Vet. Akad. Handl.*, 1774, xxxv; "The Chemical Essays of William Scheele," Beddoes Translation. London, 1786, p. 97.

* *Gilbert's Annalen*, 1822, lxxi., 107.

† *Annalen*, 1832, iii., 141

‡ *Pogg Ann.*, 1829, xv., 307.

§ *Annalen*, 1836, xvii., 69

‖ *Ann. Chem. Phys.*, 1831, xlviii., 395.

plete even after the evaporated water had been several times renewed. He also showed that ammonium formate decomposed at about 180° into hydrocyanic acid and water. Only traces of formate escaped decomposition when the distillation was carried out in a narrow tube plunged in a long column of mercury heated to 180—200°. The product of the distillation was very concentrated hydrocyanic acid.

Geiger* appears to have observed, independently of Pelouze, that when an aqueous solution of potassium cyanide is evaporated, potassium formate is contained in the residue.

The relationship of formic acid to methyl alcohol was established† in 1835 by Dumas and Peligot. These chemists found that although wood spirit could be left in contact with air without change, *e.g.*, in a badly stoppered bottle, if the vapour mixed with air was brought into contact with finely-divided platinum, heat was evolved and formic acid produced, just as acetic acid was produced under the same conditions from ordinary alcohol.

THE PHENOMENA OF PASSIVITY.‡

By MAX LE BLANC (Leipzig).

In response to the kind invitation of the Faraday Society, I take the opportunity of giving a brief survey of the phenomena of passivity, and I shall attempt to present them viewed from a uniform standpoint.

The first observations relating thereto are more remote than one usually supposes; even at the end of the eighteenth century, at the time of the discovery of galvanism, James Keir (*Phil. Trans.*, 1790, lxxx., 374), following on still earlier experiments by Bergmann, remarked that when he poured an unsaturated solution of silver in pure colourless nitric acid upon a piece of pure iron wire, a reaction did indeed take place at first, with the separation of metallic silver; but the action of the iron upon the liquid soon ceased and the silver re-dissolved. Then for several weeks the iron lay at the bottom of the vessel, apparently unchanged and bright.

It is interesting to note that Keir became aware of the instability of this peculiar condition; it was lost by scratching the piece of iron, as also by touching it with a new piece.

The phenomenon was not then further investigated until 1827, when it was re-discovered by Wetzlar (*Schweigger's Journ. f. Chemie u. Physik*, 1827, xlix., 470; l., 88, 129), who drew attention to electrochemical relations. Fechner (*Ibid.*, 1828, liii., 141) then made electrical measurements, which showed that by forming an element of iron-silver in a silver solution the iron remained electropositive so long as it possessed the power of dissolving spontaneously and reacting chemically. As soon as this power disappeared it became electronegative.

At the end of the thirties the investigation was continued by Schönbein (*Pogg. Ann.*, 1836, xxxvii., 390, 590), who published a mass of new details; especially he showed that the inactive condition of iron can be brought about by making it in a suitable manner the anode in aqueous, even dilute solutions of different oxyacids. He introduced the expression "passive," which has ever since been retained.

At this time it was known that other metals than iron could also assume this peculiar property of passivity.

Attempts to account for the phenomena of passivity have naturally been made. The discoverer himself, Keir, had thought about the matter, as can be seen from the closing words of his paper:—"The explanation of these phenomena will be attempted in the subsequent paper." This promise, however, he did not fulfil.

* *Annalen*, 1832, i., 44

Annalen, 1835, xv., 1.

A Contribution to the General Discussion on "The Passivity of Metals" held before the Faraday Society, November 12, 1913.

Fechner thought of the formation of a protective coat, but inspection by another person convinced him that the iron was so bright that, to him, oxidation seemed quite out of the question.

Faraday (*Phil. Mag.*, 1836, ix., 61) held a different opinion, and expressed himself thus:—"My strong impression is that the surface of the iron is oxidised, or that the superficial particles of the metal are in such relation to the oxygen of the electrolyte as to be equivalent to an oxidation; and that having thus their affinity for oxygen satisfied, and not being dissolved by the acid under the circumstances, there is no renewal of the metallic surface, no reiteration of the attraction of successive particles of the iron on the elements of successive portions of the electrolyte, and therefore not those successive chemical actions by which the electric current (which is definite in its production as well as in its action) can be continued."

This oxide theory, with numerous modifications, has been adopted up to quite recent times by a large number of investigators without any surer proof of its correctness having been brought. On the other hand, certain facts have become known which either cannot or only with difficulty can be brought into line with the theory of an oxide layer forming a protection for the electrode. Most important is the discovery of Müller and Königsberger (*Zeit. Elektrochem.*, 1907, xiii., 659; 1909, xv., 742), according to whom the reflecting power of iron in alkaline solutions is identical in the active and in the passive state; they proved, however, that a layer of lead peroxide of approximately molecular thickness (0·8 $\mu\mu$) deposited upon a platinum mirror greatly diminished the reflecting power of the mirror, and the optical constants of the known iron oxides and hydroxides differ only very slightly from those of lead peroxide; hence these workers both come to the conclusion that the passivity of iron is not occasioned by a coating of oxide.

Krüger ("Vortrag auf der Hauptverslg. der Deutschen Bunsen Ges. zu Breslau," 1913) has recently come to the same conclusion by measuring the reflecting powers of passive and active iron for ultra-red rays.

One may object that the hypothetical oxide may have other properties than the known oxides, but one would have to confess that such an *ad hoc* supposition would be arbitrary and improbable. The same can be said of the supposition that the layer is so extremely thin that it only just covers the surface, but cannot be detected by even the most sensitive optical method. It is indeed not comprehensible on what grounds the protective layer should be formed in just such small dimensions, for in those cases in which no one doubts the formation of oxide—as, for example, in the case of the anode treatment of lead electrodes in sulphuric acid or in sodium chromate solution—the conducting metallic oxide which covers the surface after a short time becomes easily visible to the naked eye.

Such firmly adherent anodic layers, which protect the underlying metal, are always accompanied in electrolysis by simultaneous evolution of oxygen if the electrolyte consists simply of a salt, whose anions form with the anode metal a difficultly soluble compound (Le Blanc and Bindshedler, Isenburg, Just, *Zeit. Elektrochem.*, 1902, viii., 255; 1903, ix., 275, 577). Should, however, excess of another salt be added, whose anions form an easily soluble salt with the anode metal—*e.g.*, sodium chlorate in the case of lead anodes in sodium chromate solution—there is neither evolution of oxygen nor the deposition of any firmly adhering precipitate on the anode, but a precipitate is quantitatively produced, which falls away from the electrode, which remains bare. This process has been applied for the technical production of difficultly soluble substances, such as white-lead, and it is based upon the fact that in consequence of the simultaneous action of the excess of chlorate ions nearest the electrode a layer of liquid free from chromate ions forms soon after the commencement of the electrolysis. This layer prevents the

formation of precipitate in the immediate vicinity of the electrode, and consequently also prevents any adhesion thereto.

How do *passive* electrodes behave in such cases? Nickel is passive under anodic treatment in pure potassium sulphate solution and oxygen is evolved; in pure sodium chloride solution it easily dissolves. On adding sodium chloride to the potassium sulphate solution, solution of the nickel still takes place with a moderate current density, whilst the evolution of oxygen ceases, but no detachable precipitate becomes visible. So that this observation is also unfavourable to the supposition that all cases of passivity are due to the formation of a good conducting protective layer on the electrode.

Furthermore, the strong influence of rise in temperature in restoring the activity of the metal concords ill with the oxide theory, whilst the remarkable instability of this layer must excite wonder, since it finds expression in the spontaneous return of the metal to a more or less active state when the means of bringing about the passive condition are withdrawn.

This last point has already been raised by Schönbein (*loc. cit.*) as an argument against the oxide theory of Faraday. The particular passage reads thus:—"A further and more important circumstance, to which attention must be drawn, is the fact that the iron wire, which dips in the dilute acid and remains indifferent to it, becomes attacked as soon as the electric current no longer passes through it. For instance, by leaving the wire dipping in the acid and opening the circuit in some way, there appear instantly yellowish brown streaks shooting downwards, *i.e.*, ferric nitrate. . . . It is also clear that if the passivity of the positive iron wire be due to a film of oxide upon it, then the same wire, when removed from the circuit and placed in ordinary nitric acid, should remain passive; but this is not the case."

Thus from the various facts quoted, which can also be amplified, it is evident that the hypothesis of an impervious layer, which covers the surface of the metal, thereby protecting it from contact with the electrolyte, is open to the most serious objection.

We shall therefore attempt to arrive at an understanding of the phenomena of passivity on other grounds; this brings me to the polarisation measurements for metals, immersed in their respective salt solutions, which I carried out some years ago (Le Blanc, *Abhandlungen d. Deutschen Bunsen Ges.*, 1910, No. 3). Although these measurements may seem to have little to do with the problem in hand, we shall presently see that they can be brought to bear very closely upon it.

Let us take as our basis for the calculation of the potential difference at a metallic electrode Nernst's formula—

$$E = \frac{RT}{n_e F} \log \frac{P}{p}$$

(R = gas constant; T = abs. temp.; n_e = valency of the metal; F = 96,540 coulombs; P = constant for a given metal under given conditions (the electrolytic solution pressure); p = osmotic pressure of the corresponding metal ions). Let us suppose also that the formula can be applied for any desired variable condition, so long as it be reversible; then at constant temperature polarisation, and consequently a rise in potential difference, can only occur in consequence of a change in value of P or of p. If we exclude the former by using a specified metal electrode, the electrode potential can only be changed by changing p, or, since p depends upon the concentration of the solution of metallic salt, simply by changing the concentration of the solution.

From this point of view we might expect that when employing a system: metal—a not too dilute solution of a metallic salt—metal (*e.g.*, copper-copper sulphate solution-copper), no appreciable polarisation would take place in the case of a short-timed electrolysis with a moderate current density, for under such circumstances no marked change of concentration of the electrolyte at the electrodes can occur. This expectation was fulfilled in the cases of the systems: lead-lead nitrate solution-lead; and mercury-mercurous nitrate solution-mercury; in all the other cases that were tried, anodic, and at the same time cathodic, polarisation occurred in spite of an ample ion concentration; especially was this the case in the systems: copper cupric sulphate or chloride in water-copper; silver-silver nitrate solution in water or in acetonitrile silver; iron-ferrous chloride in water-iron; nickel-nickel chloride in water-nickel. The degree of polarisation was dependent on many influences; for example, on the current density, the temperature (with rise of which it decreased), and the condition of the electrodes and solution. In many cases it could be greatly increased by addition of extremely small quantities of strychnine, brucine, gelatin, &c., and, indeed, always both at the anode and the cathode; the increase amounted to several tenths of a volt.

How can these facts be explained? Let us disregard the unlikely supposition that alternating obstructions oppose the processes of charging and discharging. Is there, however, not the possibility that the interchange of charge may be associated with a chemical reaction of changing velocity?

If we first consider the action at the anode, it is conceivable that primarily no metal ions are formed, as generally supposed, but that the electrical process consists of a discharge of negative ions and the chemical process of an interaction between the non-electrified radical and the metal. The potential difference would, according to this view, depend upon not only the concentration of the negative ions, but upon that of the separated non-electrified radical, and consequently upon the velocity with which the latter reacts upon the metal. For the smaller this is (*ceteris paribus*), the greater must the concentration become for a given current density, until the velocity of the reaction, which by the law of mass-action also increases, has become so great that in unit time as much of the radical disappears through chemical action as is produced by the electric current.

This view is certainly justified for series of solids, such as silver-silver sulphate or chloride-silver, which according to the researches of Haber and Zawadzki (*Zeit. Phys. Chem.*, 1911, lxxviii., 228) even at low temperatures show considerable polarisation at the anode; nor can any serious objection be made to its application to the series of liquids quoted above, but in the latter case we are not obliged to relinquish the usual idea of the preliminary formation of metallic ions, in order to be able to assign the observed polarisation to failing chemical reaction velocity; we need only adduce the probable extensive hydration of the metal ions (or their combination with the solvent). The process of hydration which occurs at the surface of the electrode, and whose velocity depends on different influences, must, as shown in the introduction, then follow on the formation of ions, which, when the current passes, is practically infinitely rapid. The magnitude of the potential difference is then, it should be carefully remarked, dependent only upon the concentration of the non-hydrated, free ions, and the latter again upon the velocity of hydration. In this way polarisation, which changes according to circumstances, easily explains itself—also its decrease with rising temperature, since the chemical reaction velocity increases almost without exception with rising temperature.

In a similar manner the cathodic polarisation, which in these experiments always accompanies that at the anode, can be explained. When the current passes, the free ions separate, which must, in the state of equilibrium, according to the law of mass-action, always be present in addition to the hydrated ones. Consequently a diminution in concentration and then polarisation follows, owing to the insufficiently great speed of the formation of free from hydrated ions. Indeed, the simultaneous occurrence of polarisation at the anode and the cathode finds a satisfactory explanation in this hypothesis, for both result from the same reaction: ion-hydrate $\rightleftarrows$ ion + water, which

takes place at both electrodes in opposite directions, and any catalytic influence, such as the quoted case of the addition of strychnine, must change the velocity of the reaction in either direction in the same proportion. Indeed, as has been pointed out, a simultaneous increase of polarisation was always observed at the two electrodes.

In addition to this cause, another can be considered in the case of cathodic polarisation; we may expect that the discharged metallic ion frequently does not separate as solid metal, but remains at first dissolved, forming a supersaturated solution. With increasing supersaturation polarisation must increase.

The absence of polarisation of the mercury and lead compounds points to the fact that in these cases the chemical and physical processes concerned take place with greater velocity.

It should be expressly understood that all the foregoing experiments were carried out under such conditions that the metals dissolve without evolution of oxygen under the action of equal currents according to Faraday's law, and further that polarisation is not occasioned by any ohm-resistance at the electrodes. Were this the case, polarisation would *immediately* disappear on breaking the current, whereas a gradual decline was actually observed, which could easily be followed and measured; in other words, the above-mentioned systems, which before the passage of the current possessed no e.m.f. and were unable to give a current, could do so after having first passed a current and then broken it. Hence it was proved that both at the anode and at the cathode, which could be separately examined, a condition was brought about which, at the cessation of the current, had electromotive power.

(NOTE.—The same explanation holds for the supertension which occurs at the electrodes with liberation of gas, which also has electromotive power. I mention this because recently J. W. Richards—*Trans. Faraday Soc.*, 1913, ix., 140—has erroneously attempted to characterise this supertension merely as resistance).

If we account for the polarisation here observed by this explanation of failing reaction velocity, we can go a step further and apply the same explanation to the phenomena of passivity. With passive metals ionic hydration occurs so slowly at the anode (a certain amount of solution nearly always takes place), that the concentration of free ions, and therefore the potential difference, becomes so great in a short time that visible separation of the negative radical or of oxygen can result. Qualitatively these phenomena present nothing fresh in distinction to those described before; quantitatively they are only of value when chemical polarisation has become so strong that solution of the metal practically ceases and the negative radicals (or oxygen) are separated and become visible.

From this point of view we must henceforth understand by passivity phenomena all such as result from chemical polarisation. We have seen that passivity is not the exception but the rule, and that it is not connected with oxygen-containing anions, as was supposed, but that it takes place also with chlorides and other solvents, and especially that it can also take place at the cathode.

Briefly it may be mentioned that one may ascribe the peculiar shift in valency which occurs on dissolving many metals, *e.g.*, chromium, by altering the experimental conditions, also to the changing hydration velocity of the ions of different valency.

I have thus attempted to establish as a fact that passivity phenomena are to be traced to those of reaction velocity. The reaction velocity theory can as yet afford no special information upon the conditions under which a metal becomes active or passive. Still one cannot reasonably regard this circumstance as a defect of the theory; it is rather due to the fact that our knowledge of the effect in chemical reaction velocities of outside factors is extraordinarily deficient. Thus another wide field is opened up for special research, and the work is being carried out with assiduity.

THE SCIENTIFIC WEEK.

(From Our Own Paris Correspondent).

THE UBIQUITY OF BORON.

The rarest metals and metalloids are to be found normally in the human organism, in the tissues of animals and vegetables. But the study of these bodies has been most difficult, and it is only quite recently that Prof. Armand Gautier has been able to discover and measure the tiny quantities of fluorine contained in the organs of man. M. Gabriel Bertrand, the head of one of the services of the Pasteur Institute, has just discovered that the tissues of plants and animals contain pretty appreciable quantities of boron or boric acid. And the quantitative method that he has devised in collaboration with M. Agulhon, to recognise the quantities of boron contained in divers substances, will have very important bearings on the application of the law against fraud and adulteration of food in trade. As people were ignorant of the constant presence of boron in the form of borate or some other combination in the living cellules, it was generally admitted that the boric acid found in the ashes of alimentary substances derived from plants or animals proceeded from a voluntary introduction as an antiseptic. As the dosage of this boric acid presented great difficulties, the mere qualitative research was all that was sought after; the result of this was that, up till now, the decision of the expert analytical chemist has depended almost exclusively on the greater or less degree of sensibility of the qualitative method that was employed. This way of operating is no longer admitted. The method of M. Bertrand enables one, in a few hours, to no longer confound the boric acid contained normally in the ashes of an alimentary substance with that which may have been introduced as an antiseptic. MM. Bertrand and Agulhon have thus found in a kilogrm. of the pulp of dried apricots 112·6 mgrms. of boric acid. In the same conditions they have calculated that there were 112 mgrms. per dry kilo. of the pulps of cherries, of dried figs, of strawberries, of peaches, of prunes, and in certain vegetables, such as carrots, French beans, turnips, and onions. Fifty-six mgrms. of boric acid are to be found per kilo. in English pears, black plums, apples, wild strawberries, white grapes, tomatoes, dried haricots, &c. In black grapes 225 mgrms. of boric acid have been found per kilogrm. Lastly, these two scholars have found a smaller quantity of boric acid in the muscles of the rabbit, of the lobster, of the horse, of the ox, of the pigeon, in cows' milk, and even in the egg of a hen. Like arsenic, boron is then to be found everywhere. Many shopkeepers and tradesmen have been condemned because boric acid had been found in tinned goods. In the greater part of these cases they were simply judicial errors. Henceforth it will be easy, thanks to the method of M. Bertrand, to discover and recognise which are the fraudulent goods.

ANTITYPHOID VACCINATION.

The administration of microbian products by the gastric canal, in view of obtaining a vaccinal immunisation against the corresponding affection has already tempted several experimenters. Against typhoid fever, Schitchkine has had cultures of typhic bacilli, heated to 60 degrees, injected into rabbits without succeding in vaccinating them. Prof. Courmont and Dr. Rochaix have obtained a relative immunity of the animals treated with pretty strong reactions which caused them to abandon the method. MM. Auguste Lumière and Jean Chevrotier, of Lyons, have succeeded, after a year's study, in preparing sterilised vaccines, then heated to fifty degrees, containing three microbian species in the proportion of 300 millions of Eberth's bacilli for 180 millions of coli bacilli and 120 millions of paratyphic bacilli. This vaccinal powder at the dose of three millions of micro-organisms per animal kilo. ingested in three fractions in an interval of eight days realised in guinea pigs and rabbits a sure and lasting

immunisation against typhic or paratyphic infection. Four months after their vaccination, the animals vaccinated were able to receive a mortal dose of each of the virulent cultures without showing any trouble whatever.

THE ELECTION OF PROF. CHARLES RICHET.

Prof. Charles Richet has been elected a titulary member in the section of medicine and surgery of the Academy of Sciences, in the place of the late Dr. Just Lucas Championnière. The section had presented M. Charles Richet in the first line, and in the second line according to their alphabetical order, Messrs. Bazy, Delorme, Pozzi, Quiem, and Reclus. After the first ballot, M. Charles Richet was proclaimed elected with 42 votes out of 56 voters, M. Reclus received 11 votes, M. Delorme 2, and M. Quiem 1 vote. The new Academician is a savant of the first rank. A few weeks ago he received the Nobel prize of Medicine for the year 1913, and only a few days ago the Government presented him with the scarf of a commander of the Legion of Honour. Yesterday he was appointed member of the Academy of Sciences. The son of a noted surgeon, member of the Institute and Professor of the Faculty of Medicine, Prof. Charles Richet was born in Paris in 1850. "Agrégé," or fellow of the Faculty, in 1879, he was appointed in 1887 to the chair of physiology at the Faculty of Medicine. He began to attract the attention of the learned world by the discovery of seropathy. It is, indeed, to M. Charles Richet that we owe the discovery of serums, the numerous victories of which are now well known. The first injection of serum into a man was made by the learned physiologist on December 6th, 1890. Before this, in 1888, he had tried an antituberculous serum on dogs, but without success. The second discovery due to Prof. Richet, a discovery which is revolutionising medicine and physiology, is that of anaphylaxy. In his speech, not yet published, pronounced at Stockholm in December last, M. Charles Richet made known his latest works in connection with this new road opened in the domain of serums and vaccines. It is known that anaphylaxy is a particular sensibility of the organism of animals to inoffensive doses of toxic substances especially of an albuminoid nature. Dogs having received a first injection of poison as a non-mortal dose were again injected with a small dose, three weeks or a month later. An unexpected fact then took place. Instead of being accustomed to the poison the organism of these animals had become so sensitive that this minimum dose had most terrible consequences and even occasioned rapid death. Anaphylaxy is then the contrary of mithridatism or the custom or habit of poisons. The literary and dramatic production of the learned physiologist is important. His philosophical works, such as "Love and Intelligence," his "Essay of General Psychology," his theatrical pieces such as "Socrates and Circe," his novels "Sister Marthe," the "Pain of Others," "The Search for Happiness," &c., show that M. Charles Richet is a fine and delicate "lettré."

Institute of Chemistry.—*Pass List January Examinations, 1914.*—Of eighteen Candidates who presented themselves for the Intermediate Examination, seven passed:—H. G. T. Boorman, G. A. Bracewell, R. O. Eames, J. W. Harris, D. G. Hoyle, R. G. Thin, J. Young. One Candidate presented himself for Examination in General Chemistry for the Associateship and passed:—E. Spencer. Of twenty Candidates who presented themselves for the Final Examination for the Associateship (A.I.C.), ten passed:—In Branch (*a*), Mineral Chemistry—E. D. Goddard, F. C. Guthrie, G. S. Heaven. In Branch (*c*), Physical Chemistry—C. W. James. In Branch (*d*), Organic Chemistry—R. S. G. Knight, S. I. Levy, E. Williams. In Branch (*e*), the Chemistry of Food and Drugs, Fertilisers and Feeding Stuffs, Soils, and Water—B. G. Fagan, W. Honneymann, Miss Ethel G. Mocatta.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, January 22nd, 1914.

Sir WILLIAM CROOKES, O.M., President, in the Chair.

PAPERS were read as follows:—

"*Heat Production Associated with Muscular Work: A Note on Prof. J. S. Macdonald's Paper, Proc. Roy. Soc., B, vol. lxxxvii.*" By R. T. GLAZEBROOK, F.R.S., and D. W. DYE, B.Sc.

Prof. Macdonald's results are analysed graphically by plotting, equations being obtained from curves connecting the various quantities—Heat Produced, Work Done, Mass of Individual. The average values of Heat Produced by various persons, all working at the same rate, are first plotted against Rate of doing Work; a linear relation is found, of form $H = H_0 + \frac{W}{\lambda}$, where H_0 represents Heat Produced for zero Work Done.

The values of Heat Produced are next plotted against Rate of Work for each individual; these give approximate straight lines of the same equation as above, but with constants H_0 and λ differing for each individual. These values of λ are then plotted against corresponding masses M of individuals, and again a linear relation results, of the form $\lambda = \alpha + \beta M$. In a similar manner H_0 is plotted against M, giving once more a linear relation $H_0 = a + bM$.

Collecting these equations, a complete expression connecting the quantities H, W, M, is found, viz., $H = a + bM + \frac{W}{\alpha + \beta M}$. A table and series of curves give values of H by this equation for particular values of M and W used in experiments. These give good agreement with observed values of H.

"*Chemical Interpretation of some Mendelian Factors for Flower Colour.*" By M. WHELDALE and H. L. BASSETT.

These researches deal with the Mendelian factors for flower-colour in varieties of *Antirrhinum majus*. Two varieties, ivory and yellow, are chiefly considered. Ivory is a simple Mendelian dominant to yellow and contains a factor "I" which is absent from yellow. The authors have previously identified the pale yellow pigment of the ivory variety with a flavone, *i.e.*, apigenin. In the present paper it is shown that the yellow variety contains, in addition to apigenin, another flavone pigment, *i.e.*, luteolin, which is present in the epidermis and which accounts for the deeper yellow colour of the flower. Hence the dominant ivory factor may be expressed as the power to inhibit the formation of luteolin in the epidermis.

The authors also criticise the hypothesis brought forward by Keeble, Armstrong, and Jones (*Proc. Roy. Soc.*, 1913, B, lxxxvi., 308) to account for the loss of colour both in an alcoholic solution of anthocyanin and in petals containing anthocyanin when immersed in alcohol, and the subsequent recovery of colour under various conditions. The above hypothesis postulates the existence in the petals of an oxydase and a reducing agent; the former produces anthocyanin from a colourless chromogen and the latter reverses the reaction. In the absence of water, *i.e.*, in alcohol, the oxydase is rendered inactive, but the reducing agent remains active, and the colour disappears; on addition of water, the oxydase activity is restored and the colour returns.

The authors show that the colour can be restored either to petals or solution by dry hydriodic acid gas. Also the colour returns in water in an atmosphere of hydrogen. Moreover on dilution with water, the colour is restored to the strong alcoholic solution (which presumably does not contain oxydase) after it has been heated to 100° C.

"*Determination of the Minimum Lethal Dose of Various Toxic Substances and its Relationship to the Body Weight in Warm-blooded Animals, together with Considerations Bearing on the Dosage of Drugs.*" By Prof. G. DREYER, M.D., and E. W. A. WALKER, M.D.

1. In warm-blooded animals of same species but different weights, dosage must be calculated in relation to body surface.

This result agrees with the conclusion already reached by Moore though on different grounds.

2. This statement is to be explained on the ground that concentration in plasma of any given substance administered is dependent on volume of blood circulating, which is itself proportional to body surface in any given species of animal.

3. It follows that in accurate measurement and standardisation of toxic substances and antitoxins it will now be possible to make use of animals of different weights within a given species instead of using only animals of an arbitrarily selected weight, as has hitherto been necessary.

4. Results in dosage calculated from one species of animal cannot directly be applied to another species merely by taking surface into due consideration, since tolerance and intolerance are specific characters shown to be in many cases independent of size of species concerned.

5. For the human subject, dosage, in relation to surface, works out very simply as, approximately:—

At 21 years	Full dose	At 3—4 years	$\frac{1}{4}$ dose
At 15 years	$\frac{3}{4}$ dose	At 1 year	$\frac{1}{6}$ dose
At 9—10 years	$\frac{1}{2}$ dose	In early months	$\frac{1}{10}$ dose

"*Experiments on the Restoration of Paralysed Muscles by Means of Nerve Anastomosis. Part II. Anastomosis of the Nerves Supplying Limb Muscles.*" By Prof. R. KENNEDY, M.D.

"*Variations in the Sex Ratio of* Mus Rattus *following an Unusual Mortality of Adult Females.*" By F. NORMAN WHITE, M.D.

CHEMICAL SOCIETY.

Ordinary Meeting, December 18th, 1913.

Prof. W. H. PERKIN, LL.D., F.R.S., President, in the Chair.

(Concluded from p. 57).

340. "*An Adiabatic Calorimeter.*" By FRANCIS WILLIAM GRAY.

The author described a water mantle, the temperature of which can be altered at will to prevent radiation inwards to or outwards from the calorimeter. The temperature is raised by pumping water from a hot bath through a flexible copper tube immersed in the water of the mantle. The temperature is lowered by passing tap-water through the same flexible copper tube, or, if necessary, by pumping water from a cold bath through the flexible tube. The flow of water is controlled by a system of two T-tubes and four taps. With this apparatus any rate of rise or fall of temperature likely to be required in thermochemical work can be obtained. A turbine stirrer is used for the mantle water.

341. "*The Distillation of Coal in a Vacuum.*" By MAURICE JOHN BURGESS and RICHARD VERNON WHEELER.

An account was given of distillations of coal in a high vacuum at low temperatures, and the apparatus used described.

The gaseous products of distillation only were discussed in detail, the liquid products being dealt with in a subsequent paper.

The sequence of events when coal is gradually raised in temperature in the absence of air was described, and it was shown that of part of the coal substance a decomposition point occurs at about 350°.

Fractionation of the gases by means of liquid air and solid carbon dioxide dissolved in ether was stated to have enabled propane and butane to be isolated, and the presence of pentane established by explosion analysis.

342. "*The Composition of Coal.*" By DAVID TREVOR JONES and RICHARD VERNON WHEELER.

An account was given of an examination of the liquid products of distillation of coal in a vacuum at low temperatures, from which conclusions were drawn regarding the composition of the "resinous substances" that form part of the coal conglomerate.

A description was given of the various compounds contained in the oils obtained, which consisted largely of unsaturated (ethylenic) hydrocarbons, naphthenes, paraffins, phenols (chiefly cresols and xylenols), and homologues of napthalene. Benzene, anthracene, and solid aromatic hydrocarbons were stated to be absent.

The presence or absence of free hydrocarbons in any quantity in coal was discussed, and an hypothesis put forward to account for the rapid formation of paraffins, naphthenes, &c., on distilling coal at low temperatures. It was suggested that such hydrocarbons must be present in the coal substance in such a manner that whilst, in a sense, structurally complete, some change in their state, such as can be produced by moderate heating, must take place before they can be set free.

This hypothesis, particularised for the case of the paraffins, assumes their existence in coal as alkyl groups attached chemically to another non-alkyl group, R·H, the paraffin being in what can be termed a "bound" condition, as a component part of a molecule represented by the general formula $RH-C_nH_{2n+1}$. The rapid distillation of "free" paraffins from these "bound" molecules when coal is decomposed thermally was then explained according to the following scheme:—

$$RH-C_nH_{2n+1} \rightarrow R+C_nH_{2n+2},$$

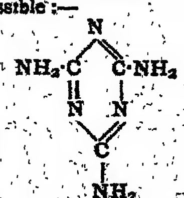
or—

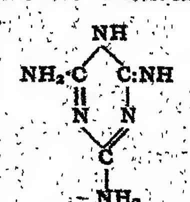
$$RH-C_nH_{2n+1} \rightarrow R+C_{n1}H_{2n1+2}+C_{n2}H_{2n2}.$$

With certain modifications the hypothesis was used to explain the appearance of naphthenes, olefines, and naphthalene homologues in coal distillates.

343. "*isoMelamine.*" (Preliminary Note). By HANS KRALL.

Four isomerides of melanamine are theoretically possible:—


I.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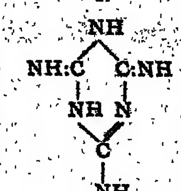
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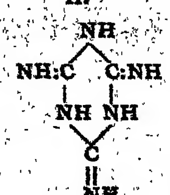

IV.

Only one of these, usually assumed to be (I.), is known. Two series of alkylmelamines are known, and are usually assumed to be derived from (I.) and (IV.). During an investigation of the action of heat on guanidine salts, a second melamine has now been obtained; it is probably formed by the polymerisation of cyanamide in its carbodiimide phase, NH:C:NH, and may be assumed for the present to be the hitherto unknown *iso*melamine (IV.).

When guanidine carbonate is heated for three hours at 180°, the residue consists of a mixture of ammeline and a substance which analysis shows to be isomeric with melamine. The former is readily dissolved by cold aqueous sodium hydroxide.

*iso*Melamine crystallises from water in ill-defined crystals, quite unlike the characteristic prisms of its isomeride. The two substances can be crystallised side by side from the same solution, so that the difference is constitutional, and not merely crystallographic.

*iso*Melamine gives rise to a chloride, nitrate, and sulphate of melamine, so that strong acids cause isomerisation. The true *acetate* can be obtained from which alkalis regenerate unaltered *iso*melamine.

Alkalis do not affect the constitution, but they induce hydrolysis more rapidly than with the normal isomeride.

At about 260° the compound decrepitates, and passes into the more stable form.

Both compounds are being further studied.

344. "*Fluorone Derivatives.* Part II. *Resorcinol-benzein.*" By Frank George Pope.

Resorcinol-benzein, as prepared by Doebner's method, consists essentially of 3-hydroxy-9-phenylfluorone. Confirmation of this result was shown by its conversion into the sodium and barium salts, and by the preparation of the acetyl derivative, whilst by the action of phosphorus pentachloride it yields 3 : 6-dichloro-9-phenylxanthonium chloride identical with the product of the reaction between 3-hydroxy-9-phenylfluorone and phosphorus pentachloride. The different varieties of resorcinol-benzein as described by H. v. Liebig (*Journ. Prakt. Chem.*, 1912, [ii.], lxxxv., 97, 241) were not obtained, neither were the anhydro-compounds described by the same author in 1908 (*Ibid.*, lxxviii., 534).

345. "*The Relation between Viscosity and Chemical Constitution.* Part VIII. *Some Homologous Series.*" By Albert Ernest Dunstan, Ferdinand Bernard Thole, and Percy Benson.

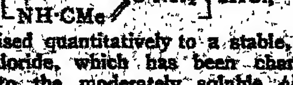
The authors have continued their work on the additive nature of log. viscosity, and have examined the viscosity of ninety-three compounds drawn from the homologous series of the fatty acids, alcohols, ethyl and methyl esters of the fatty acids, and esters of methylethycarbinol, hexan-β-ol, heptan-β-ol, octan-β-ol, and undecan-β-ol.

They find in each series that log. viscosity is additive within limits, but that the CH_2 differences vary with (1) association, (2) magnitude of the group to which the growing chain is attached, (3) molecular weight, (4) temperature.

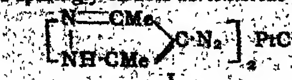
346. "*Non-aromatic Diazonium Salts.* Part III. 3 : 5-*Dimethylpyrazole-4-diazonium Salts and their Azo-derivatives.*" By Gilbert T. Morgan and Joseph Reilly.

4-Amino-3 : 5-dimethylpyrazole dihydrochloride,

can be diazotised quantitatively to a stable, very soluble diazonium chloride, which has been characterised by conversion into the moderately soluble *platinichloride* (I.) and the sparingly soluble *aurichloride* (II.) :—



I.



II.

Addition of sodium azide to the acid solution of diazonium chloride determines at once the liberation of diazo-nitrogen and the production of 4-*triazo*-3 : 5-*dimethylpyrazole*, a distinctly basic compound, which is precipitated only on neutralising the solution with sodium carbonate.

3 : 5-Dimethylpyrazole-4-diazonium chloride is even more stable than the corresponding salt from diazotised 4-aminoantipyrine ; it is not readily decomposed by boiling aqueous potassium iodide, and its capacity for azo-coupling is retained after treatment with alkali carbonates, hydroxides, thiocyanates, and cyanides.

3 : 5-*Dimethylpyrazole-4-azo-β-naphthol* dissolves very sparingly in aqueous alkali hydroxides, but is insoluble in water.

3 : 5-*Dimethylpyrazole-4-azo-β-naphthylamine* is a pale orange-brown base.

347. "*The Relative Activities of certain Organic Iodo-compounds with Sodium Phenoxide.* Part IV. *The Influence of the Solvent.*" By David Segaller.

The velocity-coefficients of the reaction between sodium phenoxide and ethyl and propyl iodides have been measured with a view of studying the influence of the solvent in this reaction.

The following solvents were employed : methyl alcohol, ethyl alcohol, propyl alcohol, *iso*butyl alcohol, *iso*amyl alcohol, and acetone.

It was shown that there is no connexion in this reaction between the dielectric constant of the solvent and the influence of the latter on the rate of the reaction. The influence of the medium is very large, the velocity-coefficient in acetone solution being more than one hundred times as large as that in *iso*amyl alcohol solution.

348. "*The Polysulphides of the Alkali Metals.* Part I. *The Polysulphides of Sodium.*" By Alexander Rule and John Smeath Thomas.

An investigation has been made of the action of sulphur on alcoholic solutions of anhydrous sodium hydrosulphide prepared by the method previously described by one of the authors (*Trans.*, 1911, xcix., 558). A vigorous reaction takes place between sulphur and the hydrosulphide in alcoholic solution, with the evolution of hydrogen sulphide and the formation of polysulphides.

Using amounts of sulphur corresponding with the di-, tri-, tetra-, penta-, and a possible hexa-sulphide, and concentrating the solution, a solid product was obtained, but only when the proportions of hydrosulphide and sulphur for the tetrasulphide were used was the product homogeneous. It consisted of the pure anhydrous tetrasulphide, which is a brownish-yellow substance, crystallising in well-defined cubes.

Below the proportions for the tetrasulphide, mixtures were obtained which contained unchanged hydrosulphide. At the pentasulphide stage the solid product is a mixture of the tetrasulphide and sulphur, whilst above that stage there is some indication of the separation of a higher polysulphide.

The course of the reaction and the probable nature of the substances present in solution before evaporation of the latter was determined by estimating the amounts of hydrogen sulphide evolved when varying amounts of sulphur were used in the reaction.

Anhydrous sodium disulphide was also obtained by reducing solutions of the tetrasulphide with metallic sodium. It is a bright yellow, micro-crystalline powder, less soluble in alcohol than the tetrasulphide.

349. "*Nitro-acids Derived from* 2 : 3-*dimethoxybenzoic Acid and* 4-*methoxyphthalic Acid.*" By John Cannell Cain and John Lionel Simonsen.

5-*Nitro*-2 : 3-*dimethoxybenzoic acid* was prepared by nitrating 2 : 3-dimethoxybenzoic acid and also by nitrating 2 : 3 *dimethoxytoluene* and oxidising the 5-*nitro*-2 : 3-*dimethoxytoluene* formed.

6-Nitro-2 : 3-dimethoxybenzoic acid (Wegscheider and Klemenc, *Monatsh.*, 1910, xxxi., 709) was synthesised as follows :—3-Hydroxy-*o*-tolyl methyl ether on nitration yields 5 : 6-*dinitro*-3-*hydroxy-o-tolyl methyl ether*, which on methylation and reduction gives 2-*nitro*-5 : 6-*dimethoxy*-m-*toluidine*. On elimination of the amino-group the resulting 6-*nitro*-2 : 3-*dimethoxytoluene* furnishes, on oxidation, the required acid.

The nitration of 4-methoxyphthalic acid yields a mixture of 3- and 5-*nitro-4-methoxyphthalic acids*, which can readily be separated. The former was also synthesised by oxidising 1-nitro-2-naphthyl methyl ether, and the latter by oxidising 5-*nitro-4-methoxy-o-xylene*.

350. "*The* p-*Nitrobenzoates of Borneol and* iso*Borneol*." By GEORGE GERALD HENDERSON and ISIDOR MORRIS HEILBRON.

In the course of investigations on the action of oxidising agents on camphene and on bornylene, the authors have more than once had some difficulty in deciding whether an alcohol present among the oxidation products was borneol or *iso*borneol. It is troublesome to obtain these compounds in a state of purity by crystallisation alone, and such of their hitherto described derivatives as are well characterised and easily prepared, for example, the hydrogen phthalates, melt at the same or very nearly the same temperatures. The authors therefore sought for some derivative of borneol and *iso*borneol by means of which the alcohols could be more easily distinguished from each other, and ultimately found that the p-*nitrobenzoates*, which can be prepared and purified without difficulty, meet this requirement.

For the preparation of the *p*-nitrobenzoates the following method gives good results:—The calculated quantity of *p*-nitrobenzol chloride is added to a solution of the alcohol in ten to fifteen times its weight of pure pyridine, and the reaction, which starts immediately, is completed by warming the solution for an hour or two on the water-bath. The pyridine is then removed by cautious addition of dilute sulphuric acid, the flask being kept cool during this operation by immersion in ice-water, and the precipitated *p*-nitrobenzoate is collected, washed with dilute sulphuric acid and with water, dried, and crystallised from alcohol. Usually one crystallisation is sufficient.

Borneol p-*nitrobenzoate*, $NO_2\cdot C_6H_4\cdot CO_2\cdot C_{10}H_{17}$, crystallises from alcohol in minute, lustrous, colourless plates, which melt at 137°. It is sparingly soluble in cold alcohol, readily so in the other common organic solvents, and insoluble in water:—

0·472 gave 19·1 cc. N_2 (moist) at 13° and 754 mm. N = 4·74.

$C_{17}H_{21}O_4N$ requires N = 4·62 per cent.

iso*Borneol* p-*nitrobenzoate* separates from alcohol in fine, colourless needles, which melt at 129°. In solubility it closely resembles the corresponding borneol ester:—

0·559 gave 22·5 cc. N_2 (moist) at 12° and 760 mm. N = 4·78.

$C_{17}H_{21}O_4N$ requires N = 4·62 per cent.

The ultra-violet absorption spectra of these esters were found to be identical, each compound, in M/10,000-solution, showing a shallow band with head at 1/λ 3080.

The esters are readily hydrolysed when heated with dilute aqueous sodium hydroxide under reflux. The liberated alcohols were distilled in a current of steam, collected, dried, and crystallised from light petroleum. The purified borneol was found to melt at 208° and the *iso*borneol at 217°; the melting point of the former is the same as, but that of the *iso*borneol three degrees higher than, that formerly recorded.

351. "*The Identity of the Supposed β-2 : 5-Dimethylpiperazine*." By WILLIAM JACKSON POPE and JOHN READ.

The authors have continued the examination of the substances described as *a*- and *β*-2 : 5-dimethylpiperazine, and now show that the behaviour of the *β*-isomeride can only be explained on the assumption that it is *cis*-2 : 4-dimethylpiperazine; it is further concluded that the *a*-compound is *trans*-2 : 5-dimethylpiperazine.

352. "*Oxidation of the Anhydrides of 1 : 1-Didhydroxy-dinaphthyldialkylmethanes*." (Preliminary Note.) By HEMENDRA KUMAR SEN-GUPTA.

This investigation has been undertaken with the object of ascertaining the constitution of some of the condensation products of *a*-naphthol with ketones, as also of synthesising some naphthaxanthone derivatives. The *anhydride* of *β*-1 : 1-*dihydroxydinaphthylpropane*, $\frac{CH_3}{CH_3}>C<\frac{C_{10}H_6}{C_{10}H_6}>O$, yields, on oxidation by chromic acid, two products, namely, (i.) an orange *compound*, $C_{24}H_{16}O_3$, crystallising in thin, soft needles, and melting at 287°; and (ii.) a golden-yellow *compound*, $C_{24}H_{16}O_4$, crystallising in lozenges and melting at 245°. The latter gives on reduction a *dihydroxy*-derivative, $C_{24}H_{18}O_3$ (m. p. 252—253°); its *diacetyl* derivative crystallises in needles and melts at 241—242°. The *anhydride* of *γ*-1 : 1-*dihydroxydinaphthylpentane*, $\frac{Et}{Et}>C<\frac{C_{10}H_6}{C_{10}H_6}>O$, similarly yields a deep red *compound* crystallising in plates and melting at 221°. The constitution of these products are being studied.

353. "*The Relation of Uranous Salts to Thorium*." By ALEXANDER FLECK.

If the electrons expelled in radioactive change arise from the same part of the atom in which the electrons governing electrochemical change of valency exist, it should follow that the chemical properties of the uranous and thorium ions are identical. By reducing a mixture of thorium and uranyl salts by nascent hydrogen and then treating the reduced liquid fractionally with a precipitant, it was found that although the properties of thorium and uranium in the quadrivalent condition are very similar, yet there is a distinct difference in their chemical nature, and they can be separated from one another by fractional precipitation. In carrying out the examination of their properties it was necessary that the precipitation, filtration, and other operations should be performed without air coming in contact with the reduced liquid.

As a result of these experiments the conclusion was drawn that the electric charges on the *a*- and *β*-particles must arise from the nucleus of the atom, and that electrons may be added to or withdrawn from the external ring of electrons, thereby increasing or diminishing the valency of the atom.

354. "*The System : Xylene—Alcohol—Water*." By ALFRED HOLT and NORMAN MURRAY BELL.

The authors have determined the data of the varying miscibility of xylene, alcohol, and water at different temperatures, also the position of the tie-lines which give the composition of the conjugate solutions.

The extent to which xylene is separated from its solution in alcohol by the addition of water has also been examined, as also the composition of mixtures of the three liquids which possess the same specific gravity.

355. "*Interaction of Glycerol and Oxalic Acid*." By FREDERICK DANIEL CHATTAWAY. (This paper was read at the meeting on December 4th, 1913).

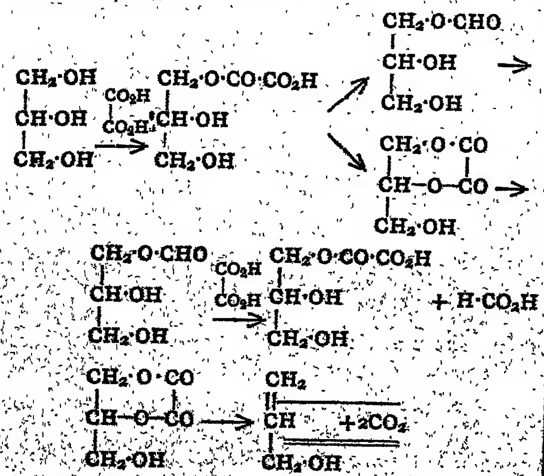
The explanation usually given in the text-books of the reactions occurring when glycerol and oxalic acid are heated together, and commonly employed in the laboratory preparation of formic acid and of allyl alcohol, is fundamentally incorrect.

The true explanation is the obvious one. The oxalic acid acts on glycerol as it does on other alcohols, and produces an acid and a normal oxalate. The former, like all such compounds, is unstable at a slightly elevated temperature, and decomposes when this is reached into carbon dioxide and monoformin. The fresh oxalic acid added displaces the formic acid from the latter, and the cycle of operations repeats itself.

The more complicated reaction which goes on when the first product of the interaction of glycerol and oxalic acid is rapidly heated, until evolution of carbon dioxide ceases and then at a much higher temperature recommences with simultaneous production of allyl alcohol, is the decomposition at the high temperature of the normal ester, which is produced from the acid ester by a repetition of the ester formation, into carbon dioxide and allyl alcohol.

The main reactions concerned in the production of

formic acid and of allyl alcohol should therefore be formulated, thus:—



and not as is at present invariably done.

NOTICES OF BOOKS.

Rays of Positive Electricity and their Application to Chemical Analyses. By Sir J. J. Thomson, O.M., F.R.S. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1913.

The publication of this book has been awaited with great interest both by physicists and chemists who recognise the remarkable possibilities of Sir J. J. Thomson's new method of analysis, and the account of the work which has been done in the Cavendish laboratory during the past seven years will, it is to be hoped, induce many other workers to enter the new field of research. The method is in some respects more powerful even than spectrum analysis, and the technique is not specially difficult. In the book the experimental details and the apparatus employed are described, and some of the photographs which have been obtained are reproduced. Some account is given of the researches of Stark on the Doppler effect of positive rays, and of Gehrcke and Reichenheim's work on the positive rays starting from the anode, and the nature of X_3, the substance giving the "3" line is shortly discussed. The author considers that the evidence points to the conclusion that X_3 is triatomic hydrogen H_3, which appears to be more stable than any known allotropic form of an element.

Photo-electricity. By H. Stanley Allen, M.A., D.Sc. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1913.

A hearty welcome will undoubtedly be accorded to this book, more particularly since, with the exception of Sir J. J. Thomson's "Conduction of Electricity through Gases," it is the only one dealing with photo-electricity which has been published in the English language. The author believes that further investigation in this sphere may lead to the reconciliation of the quantum theory with the undulatory theory of light, and he gives a quite unbiassed account of the phenomena and theories of photo-electricity. The book is written for fairly advanced students, and does not go into elementary details. An introductory chapter gives a very clear historical review of the whole field of research, and outlines the plan of the book. The work of Stark and Lenard on fluorescence and phosphorescence is fully treated for the first time in an English text-book, and the results of the work of the author and others upon photo-electric fatigue is well summarised.

The Microscopic Analyses of Metals. By Floris Osmond. Edited by J. E. Stead, D.Met., F.R.S., F.I.C. Second Edition, revised and corrected by L. P. Sidney. London: Charles Griffin and Co., Ltd. 1913.

The second English edition of this work is practically a reprint of the original translation with a few corrections of minor details, the author having expressed the wish shortly before his death that no fundamental alterations should be made in the text. Some fresh matter has, however, been added by the editors. This includes a translation of an essay by Osmond and Cartaud on polishing, and also some notes on the practical applications of metallography, and chapters on segregation in steel and on the macrostructure of steel, by Dr. J. E. Stead. The illustrations, which are an important feature of such a book as this, are very numerous and are well reproduced.

Seventh Annual Report of the Metropolitan Water Board. By Dr. A. C. Houston.

The seventh annual report on the results of the chemical and bacteriological examination of the London waters for the twelve months ended March 31st, 1913, contains abstracts of the important features of previous reports, and gives statistics of supply and short accounts of the research work which has been done in the Board's Laboratory. The Director has to report that the number of complaints from consumers showed a very marked increase as compared with those of previous years, and he admits that they were quite justifiable. They were confined almost entirely to districts supplied with water from the Staines reservoirs, where excessive development of Tabellaria frequently took place.

A New Era in Chemistry. By Harry C. Jones. London: Constable and Co., Ltd. 1913.

The author of this book has produced an interesting and pleasantly written account of the new era in chemistry, which he dates from the year 1887, when some of the most important work of van 't Hoff and Arrhenius was first published. The author has already shown in earlier books that he possesses to a marked degree the faculty of making comparatively difficult subjects easily understandable by readers who do not possess a very deep knowledge of physics and chemistry, and in this book he gives a readable account of some of the most important developments in general chemistry in the last quarter of a century. He has had a personal knowledge of many of the men who have been instrumental in bringing about the new era, and had moreover the probably unique experience of working as a student under van 't Hoff, Arrhenius, and Ostwald. Of these men, and of other great scientists, he gives many personal reminiscences and anecdotes, and the strong human note in the book will inevitably make it appeal to the student. From a scientific point of view the material is well chosen, and the short explanations appear to be always accurate and clear.

Reinforced Concrete Railway Structures. By J. D. W. Ball, Assoc.M.Inst.C.E., A.C.G.I. London: Constable and Co., Ltd. 1913.

This book contains a thoroughly practical exposition of the principles upon which the design and construction of structures made of reinforced concrete depend, and is intended more particularly for the use of the railway engineer. A special feature of the text is the great number of worked out examples, and the author has endeavoured to limit the formulæ given to those which are absolutely essential and to simplify them as far as possible, while the curve diagrams should greatly facilitate many calculations.

Organic Chemistry for Students of Medicine. By James Walker, LL.D., F.R.S. London: Gurney and Jackson. Edinburgh: Oliver and Boyd. 1913.

This book is intended for the use of students of medicine who are usually able to devote only a very short time to

the study of chemistry, and yet need to have a fairly detailed knowledge of some of the more complicated substances. In such circumstances much the best plan is for them to base their work upon a text-book such as this, in which substances of medical interest only are included. After a short chapter dealing with methods of determining melting-points and boiling-points, elementary analysis, &c., the author introduces the study of methane and some of its simple derivatives by a brief discussion of the distillation of wood. Thence he passes to a very short outline of the chemistry of the carbohydrates and alcoholic fermentation, and so on to more complicated compounds of the fatty series. In the same way the distillation of coal forms the introduction to the chapters on the aromatic derivatives. Nitrogen compounds are not introduced until the later part of the book. The division of the text into short sections does much to lighten the student's difficult task, and the brief discussions of the constitution and properties of various groups of important compounds such as alkaloids and proteins are admirably clear and quite sufficient for their purpose.

Handbook on Sanitation. By George M. Price, M.D. Third Edition. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1913.

This book contains an outline of the theory and practice of sanitation, the latter being discussed entirely from the American point of view. It is divided into three parts, the first of which deals with sanitary science. In this part the chapter on ventilation has been entirely re-written in the third edition. The second part gives an account of the applications of the principles of sanitation, and the construction and sanitation of tenements, private houses, factories, &c., are described in it, while sections on the hygiene of foods and on disinfectants are included. The last part of the book deals with the duties of inspectors, but since England is decidedly ahead of America with regard to the training provided for inspectors and the qualifications required of them, this section will be of very little use to the English student.

Underground Waters for Commercial Purposes. By Frank L. Rector, B.S., M.D. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1913.

The mineral water trade of New York, although as yet only in its infancy, is gaining rapidly in importance and volume, and hence the author of this little book thought that it might be useful to compile an account of all the literature dealing with the use of underground waters and springs for commercial purposes which has been published recently in America. The book gives short outlines of the chemical, bacteriological, and microscopical examination of water. These descriptions are sufficiently full and clear to give the reader a good grasp of the general principles involved in the various operations, but are not detailed enough to be used as a guide to the actual work in the laboratory.

The Journal of the Society of Dyers and Colourists. December, 1913.

This journal contains a very interesting paper read before a joint meeting of the Manchester Sections of the Society of Dyers and Colourists and the Society of Chemical Industry by Mr. Julius Hübner on "The History of Dyeing." Every student of technology is the better for some knowledge of the history of his special branch, but cannot as a rule devote more than a very short time to the study, and a *résumé* such as this is invaluable for stimulating his interest in the development of modern theories and practice. The lecturer made a careful study of all the original publications to which he could get access dealing with the very early history of dyeing in the East and elsewhere, and gave some very quaint recipes and illustrations, closing his remarks with the end of the 17th century.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Bulletin de la Société Chimique de France,
Vol. xiii.-xiv., No. 23, 1913.

Determination of Sulphates in Wine by Physico-chemical Volumetric Method.—Paul Dutoit and Marcel Duboux.—The volumetric determination of the sulphates in wine with N/4-baryta as reagent, and determining the conductivities in order to ascertain the end-point of the reaction, is more accurate than the gravimetric method. It is not affected by the presence of salts of calcium, magnesium, &c., nor by tartaric or malic acids.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xlvi., No. 14, 1913.

Boron Hydrides.—Alfred Stock, Kurt Friederici, and Otto Priess.—The following compounds of boron and hydrogen have been prepared:—1. B_2H_6. Obtained by heating B_4H_{10}. Melting-point, $-169°$; boiling-point, $-87°$. Very easily decomposed by water, otherwise stable. 2. B_4H_{10}. Obtained by fractionating the gas resulting from magnesium boride and acid. Melting-point, $-112°$; boiling-point, $+16°$. Very easily decomposes to give other boron hydrides. Slowly decomposed by water. 3. Liquid colourless fraction of tension about 20 mm./0°. Obtained like 1. Very unstable, polymerises to yellow solid compounds. Possibly contains B_6H_{12}. 4. B_6H_{12}. Like 2 from the raw gas. Tension 10 mm./0°. Very easily decomposed by water. 5. $B_{10}H_{14}$. Obtained like 1 and by heating B_2H_6. Melting-point, 99·5°. Volatilises undecomposed. Soluble in CS_2. Insoluble in water. Gives yellow solution with caustic soda. 6. Non-volatile colourless hydride, soluble in CS_2. Obtained like 1. Probably contains 12 atoms of boron in the molecule. Stable towards water. Gives yellow solution with caustic soda. Gives 7 on heating. 7. Non-volatile yellow hydride, insoluble in CS_2. Obtained like 1 and by heating 6. Contains about 4H atoms to 5 atoms of B. Dissolves undecomposed in water. 8. Liquid hydride which volatilises with difficulty. Obtained by heating 6. 9. Colourless, non-volatile hydride insoluble in CS_2. Obtained by heating B_2H_6; gives white crystals with water, yellow solution with caustic soda. 10. Brown hydrides resembling boron, and poor in hydrogen. Obtained by heating 7 to a higher temperature. Nearly all these hydrides give new compounds when they react with water or alkalis. Thus boron resembles carbon in its power of yielding compounds.

Behaviour of Radio-elements towards Precipitants.—Kasimir Fajans and Paul Beer.—With very few exceptions a radio-element is precipitated from a very dilute solution with a precipitate of an ordinary element, when the precipitation takes place in conditions in which the radio-element would separate if it were present in a weighable amount. The fact that this rule holds good universally shows that the behaviour of the radio elements in precipitation reactions is much less affected by abnormal adsorption phenomena than has been supposed.

No. 15, 1913.

Arseno-stibino and Arsino-bismutho Compounds.—P. Ehrlich and P. Karrer.—Stibine oxides and dichlorides and other inorganic antimony salts of the trivalent metal readily react with arsines to give arseno-stibino compounds, and bismuth trichloride behaves similarly. The condensations occur very easily at the ordinary temperature when the methyl-alcoholic solutions are mixed. The arseno-stibino compounds are very stable, with properties resembling those of the arsenious derivatives. They are usually yellowish or dark brown. The bismuth compounds

are very unstable, and are decomposed when boiled with water. They are black in colour.

Quantitative Investigations of the Absorption of Ultra-violet Rays by Saturated and Unsaturated Ketones and Aldehydes of the Fatty Series.—Jean Bielecki and Victor Henri.—The absorption curves of aldehydes and ketones can be analysed into "elementary absorption curves." With the aldehydes two elementary curves are obtained, one corresponding to the carbonyl and the other to the alkyl. With the ketones three curves are obtained, namely, the same elementary curve of the carbonyl and two curves corresponding to the two alkyls. In the absorption of rays of different wave-lengths the electrons sometimes of one of the atomic groups, and sometimes of another, come into play. The absorption is produced by only one part of the whole molecule, and this part alters with the wave-length.

Atti della Reale Accademia dei Lincei.
Vol. xxii. [ii.], No. 9, 1913.

Compounds of $CdSO_4$ with Li_2SO_4, Na_2SO_4, K_2SO_4.—G. Calcagni and D. Marotta.—$CdSO_4$ forms no compound with Li_2SO_4. With Na_2SO_4 it gives three compounds, viz.:—$3CdSO_4.Na_2SO_4$, $CdSO_4.Na_2SO_4$, and $CdSO_4.3Na_2SO_4$. With K_2SO_4 it forms two compounds, both previously unknown, $3CdSO_4.K_2SO_4$ and $2CdSO_4.K_2SO_4$.

Phototropism of Hydrazones.—F. Bovini.—The author has prepared the following hydrazones:—Phenyl, *p*-tolyl, β-naphthyl, and diphenyl hydrazones of acetophenone; phenyl, *p*-tolyl, β-naphthyl, diphenyl, methylphenyl, and benzylphenyl hydrazones of benzophenone. None of these is phototropic, and apparently the presence of an aldehyde hydrogen is necessary in order that a hydrazone may exhibit phototropism. The phenomenon is not manifested if the hydrogen is replaced by any radicle.

MISCELLANEOUS.

Royal Institution.—A General Meeting of the Members of the Royal Institution was held on the 2nd inst., the Duke of Northumberland, K.G., President, in the Chair. The Right Hon. Lord Avebury, Mr. H. A. Humphrey, Dr. Gerald Moody, and Mr. A. Ross were elected Members. The special thanks of the Members were returned to Lady Huggins for her present of a protrait of the late Sir William Huggins, and to Mr. Bence Jones for his present of three boxes containing some relics of Faraday. The Honorary Secretary announced the decease of Sir David Gill, K.C.B., and Mr. H. F. Makins, Members of the Royal Institution, and resolutions of condolence with the relatives were passed.

Institute of Chemistry.—Mr. William MacNab, F.I.C., will deliver the first of two lectures on "Explosives," on Thursday, February 26, 1914, at 8 p.m., at King's College Strand. *Syllabus of Lecture*:—Short historical sketch of manufacture and use of explosives; comparatively little change or progress made until about fifty years ago; since then great and varied development. Field of available bodies and mixtures as explosives greatly widened by introduction of detonators. General considerations of the character of explosive decompositions. Two modes of explosion—combustion or deflagration and detonation; means of initiating each mode. Velocity of explosion wave in detonated explosives. Conditions under which the result of an explosive decomposition can be foreseen from theory; conditions which interfere with theoretical conclusions and necessitate experimental determination. Limitations of experimental methods. Heat developed, volume and composition of gases, and pressure produced; effect of pressure on composition of gases. Theoretical temperature reached on explosion; experimental attempts to measure it; need for further work. Sensitiveness of explosives—means of increasing or diminishing it. Consideration of certain types of explosives in general use. Qualities which they should possess. Methods of testing explosives.

South-Western Polytechnic Institute, Manresa Road, Chelsea, S.W.—A course of six lectures "On Milk," followed by practical work, will be delivered by Prof. A. Harden, D.Sc., F.R.S. (of the Lister Institute), on Thursday evenings at 7.30 o'clock, commencing February 5, 1914. The syllabus is as follows:—*Chief Properties of Milk.*—The Constituents of Milk; Milk-sugar, Fat, Proteins, Salts; Specific Gravity; Analysis of Milk; Detection of Adulteration; Effect of Heat on Milk; Dietetic Value of Milk. *Bacteria in Milk.*—General Life History of Bacteria; Methods of Detection, Enumeration, and Isolation; Mode of Reproduction and Nutrition; Occurrence in Air, Water, and Soil, and in the Animal Body; the Nature and Source of the Bacteria in Milk; Suspended Matter in Milk; Bacteriological Standards of Purity. *Changes Produced in Milk by Bacteria.*—Curdling of Milk by Acid and by Rennet; Influence of Temperature and Preservatives. *Spread of Disease by Milk.*—Diphtheria; Scarlet Fever; Typhoid; Summer Diarrhœa; Tuberculosis; Tracing of Epidemics to Milk Supply. *Preventive Measures.*—Importance of Cleanliness; Refrigeration; Methods of Distribution; Sterilised and Pasteurised Milk. *Practical Work.*—A Practical Class will be held immediately after the lecture, the work of which will include simple methods of ascertaining the Composition of Milk, the Detection of Impurities and Preservatives in Milk, and the Bacteriology of Milk.

MEETINGS FOR THE WEEK.

Tuesday, 10th.—Royal Institution, 3. "Animals and Plants under Domestication," by Prof. W. Bateson, F.R.S., &c.

Wednesday, 11th.—Royal Society of Arts, 8. "History of Colour Printing," by R. A. Peddie.

Thursday, 12th.—Royal Institution, 3. "Types and Causes of Earth Crust Folds," by Prof. Sir T. H. Holland, F.R.S.

— Royal Society of Arts, 4.30. "Khorassan, the Eastern Province of Persia," by Major Percy Molesworth Sykes, C.M.G., &c.

— Royal Society. "Chemical Action that is Stimulated by Alternating Currents," by S. G. Brown. Effect of the Gangetic Alluvium on the Plumb-line in Northern India," by R. D. Oldham. "Origin of Black Body Radiation," by G. W. Walker. "Transmission of Electric Waves along the Earth's Surface," by H. M. Macdonald. "Transparence or Translucence of the Surface Film produced in Polishing Metals," by G. T. Beilby. "Method of avoiding Inaccuracy due to Weight Errors in 'Fixing' a Gold Coinage Standard Trial Plate," by A. O. Watkins. "A Thermomagnetic Study of the Eutectoid Transition Point of Carbon Steels," by S. W. J. Smith and J. Guild. "Note on Osmotic Pressure," by W. R. Bousfield.

Friday, 13th.—Royal Institution, 3. "Production of Neon and Helium by Electric Discharge," by Prof. J. Norman Collie, F.R.S., &c.

— Alchemical Society, 8.15. (At International Club, Regent Street, S.W.). "Some Notes on the Doctrine of the First Matter, with special reference to the Works of Thomas Vaughan," by Sijil Abdul-Ali.

Saturday, 14th.—Royal Institution, 3. "The Electric Emissivity of Matter," by J. A. Harker, F.R.S., &c.

THE CHEMICAL NEWS.

VOL. CIX., No. 2829.

THE ESTIMATION AND DISTINCTION OF OZONE, NITROGEN PEROXIDE, AND HYDROGEN PEROXIDE AT HIGH DILUTIONS.

By J. N. PRING, D.Sc.

THIS research was undertaken with a view of establishing some method whereby an analytical estimation and distinction of these gases could be made when present in very small quantities. The immediate purpose for which this method was required was in order to make analyses of air at high altitudes for these substances. It was necessary to employ some stable reagent which would react rapidly and quantitatively with these gases, and which could be used in small vessels attached to balloons, and also applied in mountain districts.

No conclusive method has yet been devised which would satisfy these requirements.

After a number of experiments it was found that a concentrated aqueous solution of pure potassium iodide was the only reagent which gave satisfactory results in determining ozone and nitrogen peroxide, while the use of titanium sulphate in sulphuric acid was the only satisfactory means of detecting traces of hydrogen peroxide.

It was found that the potassium iodide solution reacts with ozone, even when the gas is present at high dilutions, with great rapidity. This is also the case at temperatures as low as -50°, when the gas is passed *over the surface of* the solid reagent. As the reaction which takes place between ozone and potassium iodide is known to be very complex, the conditions were investigated for the distinction of this gas from other possible reacting gases which are present in the atmosphere.

A. *Action of Ozone on Potassium Iodide.*

It has been found that in a neutral solution this reaction gives rise to a large number of substances, including free iodine, potassium hypoiodite, iodate, periodate, hydrate, and peroxide (*cf.* Garzarolli-Thurnlackh, *Monatsh.*, 1901, xxii., 955; Brunck, *Ber.*, 1900, [2], xxxiii., 1832; Pechard, *Comptes Rendus*, 1900, cxxx., 1705).

An estimation of hypoiodite and free iodine, on the one hand, can be made in presence of the other compounds by titrating with sodium thiosulphate. If the solution is then acidified, the iodate and periodate are decomposed with liberation of iodine, and are thus readily estimated by again titrating this with thiosulphate. In the present work the measurements thus obtained were later compared with those given by hydrogen peroxide and nitrogen peroxide.

Ozonised oxygen was prepared by heating potassium permanganate in a combustion tube, and, after drying, passing the oxygen generated through Siemens tubes, and then collecting over distilled water in a gas holder of 10 litres capacity. Before filling with oxygen the whole apparatus was first carefully exhausted so as to ensure the absence of nitrogen and water vapour.

Measured volumes of this gas were then passed through, or over the surface of, the reagent, consisting of equal weights of potassium iodide and water contained in a small wash-bottle. The resulting solutions were then analysed by titration with N/100 or N/1000 sodium thiosulphate, and, after removal of the free iodine, the iodate was estimated as described above. The potassium hydrate was estimated in a separate sample by titration with N/1000 sulphuric acid.

Experiments were made with the gas at different concentrations by progressively diluting the gas in the holder by means of air which was drawn through a hot alkaline solution of potassium permanganate to remove any impurity which would react with the ozone.

TABLE I.—*Reactions at Room Temperature.*

Volume of gas (cc.).	Conc. of ozone, volume per cent.	Mgrm. equiv., calculated on total volume of reagent. Free iodine (+KIO).	Iodine as iodate (+periodate).	Potassium hydrate.	Ratio, free I_2 to I_2 as iodate
10	4·03	0·0105	0·0255	0·009	1 : 2·4
After standing 12 days		0·0137	0·024	Nil	
5	2·86	0·0052	0·00755	Nil	1 : 1·5
100	2·17	0·0438	0·150	0·028	1 : 3·5
After standing 12 days		0·0633	0·168	0·006	
4000	1·4	0·127	5·0	0·015	1 : 39·2
1000	0·90	0·288	0·570	0·012	1 : 2·5
After standing 15 hours		0·331	0·492	0·026	1 : 1·4
50	0·49	0·0066	0·0152	0·0048	1 : 2·3
After standing 12 days		0·0077	0·0142		
500	0·20	0·054	0·037	0·001	
2000	0·10	0·120	0·073	0·007	1 : 0·60
After standing 15 hours		0·183	0·074	0·008	1 : 0·41
150	0·02	0·0028	0·00047	Nil	1 : 0·16
After standing 12 days		0·0019	0·0016	Nil	
1000	0·016	0·012	0·0027	0·008	1 : 0·23
After standing 12 days		0·014	0·0032	Nil	
6500	0·00062	0·0040	Nil	Nil	1 : 0

TABLE II.—*Reaction at Low Temperatures.*

Temp. of reagent.	Volume of gas (cc.).	Conc. of ozone, volume per cent.	Mgrms. equiv., calculated in total volume of reagent. Free iodine (+KIO).	Iodine as iodate (+KIO_4).	Potassium hydrate.	Ratio free I_2 to I_2 as iodate.
-22°	4000	0·014	0·041	0·011	0·008	1 : 0·27
-28°	6000	0·0085	0·006	0·040	0·001	1 : 6·7
-53°	6500	0·0027	0·0027	0·0150	Nil	1 : 5·4
-55°	1200	0·0045	0·0012	0·0037	Nil	1 : 2·9
-59°	1750	0·0110	0·0041	0·0130	Nil	1 : 3·1

It was found that after a dilution of 1 part in one million it was no longer possible to detect the ozone. This is probably due to the destruction of the last traces by residual impurities in the diluent air. It is noteworthy to recall here the well-known fact that at a dilution of 1 part in 500,000 the gas possesses a decided odour, so that the smell constitutes one of the most delicate tests for this gas.

The results of the measurements made are given in Tables I. and II. The volume of the reagent used in the wash-bottle was in each case 5 cc. Since the cryoscopic point of potassium iodide solution is -24°, measurements below this temperature were made by leading the gas over the surface of the solid reagent. In these cases the reaction vessel was always joined in series with a second vessel containing liquid reagent through which the gas issuing from the first vessel was made to pass. It was found in every case that more than half of the ozone was removed by merely passing over the surface of the solidified reagent in the first vessel.

For the analysis of the liquid, 2 cc. were always withdrawn. In some cases a long interval was allowed to lapse before conducting the titration in order to see the

change on standing. The concentration of the ozone was calculated afterwards from the analyses of the reagent There is some doubt whether the iodine liberated after using a neutral solution and then acidifying, is an exact measure of the amount of ozone (*cf.* Brunck, *loc. cit.*; also Ladenburg and Quasig, *Ber.*, 1901, [1], xxxiv., 1184), but in any case the approximation is sufficiently close for the present purposes.

The results of these measurements establish the following points:—

1. In the reaction between ozone and potassium iodide, the ratio of iodate (+periodate) to free iodine (+hypoiodite) increases with the total amount of ozone which is passed through the reagent, as has been pointed out by Garzarolli-Thurnlackh (*loc. cit.*).

The important result shown in the present work is that, through some operation of mass action, this ratio is also increased in a very marked manner with the concentration of ozone per unit volume even when the same total quantity of ozone is passed. At some point between 160 and 6 parts of ozone in one million of air no iodate is formed on further dilution, but only free iodine and hypoiodite.

However, at temperatures below $-24°$, when the reagent is completely solidified, this relationship no longer applies, as in these cases the smallest quantity of ozone gives more iodate than free iodine (+hypoiodite).

2. On allowing the reagent, which had been exposed to ozone to stand, a slow change took place, resulting in the cases of the more concentrated products, in a considerable increase in the quantity of free iodine, while any free alkali present gradually disappeared. This change is explained by reactions which have been found to take place between potassium iodide on the one hand, and peroxide and periodate (*cf.* Pechard and Brunck, *loc. cit.*).

When only small quantities of ozone have reacted, these changes with time are comparatively small, and need not be considered when the reagent is applied for approximate atmospheric measurements.

3. It is seen that the quantity of potassium hydrate formed is very much lower than the equivalent of iodine and hypoiodite present. With very dilute gas the amount of alkali liberated is too small to detect with phenolphthalein. It would appear from these results that very dilute ozone reacts with potassium iodide to give hypoiodite or some oxygen compound lower than iodate, and that this compound is in equilibrium with a small quantity of iodine.

It is apparent from this that the method of using potassium iodide and litmus-papers, whereby the hydrate formed colours the paper blue, is quite inapplicable for quantitative measurements.

B. *Reaction between Potassium Iodide and Nitrogen Peroxide.*

Oxides of nitrogen, for the purpose of these measurements, were prepared by acting on nitric acid with copper and admitting a small quantity of the gas generated to a gas-holder, together with a large excess of air, where it would become oxidised to the peroxide. Measured volumes of this gas were then drawn by means of an aspirator through the reagent contained in a small wash-bottle. The reagent was then analysed as in the earlier cases. It was found that after the addition of acid to decompose the iodate, the end-point in the titration with sodium thiosulphate was not very definite. Thus, after once removing the iodine from the acidified solution, a further quantity gradually appeared. This is caused by the nitrous acid —which remains after the reduction of the nitric acid or nitrogen peroxide—being again oxidised by the air. In this way it behaves as a catalyst leading to a gradual decomposition of the potassium iodide by atmospheric oxygen.

In the results of the measurements which are tabulated below, the quantity of iodine found in the successive titrations after definite intervals of the acidified solutions are given.

The tables also show the ratio of iodate to free iodine formed directly when nitrogen peroxide reacts with neutral potassium iodide. These measurements could only be made with the highly diluted gas on account of the catalytic effect mentioned above with the more concentrated gas. As in the measurements with ozone, the reagent used in each case consisted of 5 cc. of equal weights of potassium iodide and water, 2 cc. were withdrawn for the analysis. After removal of the free iodine by sodium thiosulphate, 5 cc. of N/10 hydrochloric acid were added, and the liberated iodine again titrated.

Volume of gas (cc.).	Conc. of nitrogen peroxide (per cent).	Free iodine, (mgrm. equiv. in total reagent).	Interval between successive titrations.	Combined I_2 (as KIO_3, KIO_4) mgrm. equiv. in total reagent.	Ratio combined iodine to free iodine.
		A. *Room Temperature.*			
1000	0·0033	0·0004		0·0011	1 : 2·75
			5 hours	0·00616	
			65 hours	0·0151	
3000	0·0024	0·00084		0·0025	1 : 2·98
			21 hours	0·0084	
6000	0·0017	0·0007		0·0038	1 : 5·4
			25 mins.	0·0063	
		B. *Temperature* $-50°$.			
8000	0·0008	nil		0·0028	0 : 1
12000	0·00025	0·00028		0·00112	1 : 4

It is seen from these results that the presence of small quantities of oxides of nitrogen can be detected when accompanied by highly diluted ozone, since the former gas alone gives potassium iodate when reacting with iodide. Moreover, the catalytic property of nitrogen peroxide in continuously liberating iodine from an acidified solution of potassium iodide provides a characteristic and very delicate test for this gas.

C. *Reaction between Hydrogen Peroxide and Potassium Iodide.*

The reactions brought about in this case have not been conclusively investigated hitherto, but it is known that on adding hydrogen peroxide to potassium iodide solution at first no visible reaction occurs, but afterwards a slight liberation of iodine results, followed by effervescence and evolution of oxygen.

In the present work measurements were made, in some cases by passing the vapour of hydrogen peroxide into potassium iodide solution, and in others by adding a solution of the former to the latter. Estimations of the reagent were then made for iodine, alkali, and iodate.

It was found that on gradually increasing the amount of hydrogen peroxide that the free iodine present (including hypoiodite) soon approached a limiting value. The relative quantity of free alkali formed was in all cases found to be much less than corresponded to the reaction $2KI+H_2O_2=2KOH+I_2$.

It was found that no trace of iodate (or periodate) was given in any case.

The conclusion derived from these analyses is that potassium hypoiodite is the main product of the reaction, and that this then reacts with more hydrogen peroxide according to the equation $KIO+H_2O_2=KI+H_2O+O_2$. So that the main reaction, when a certain concentration is reached, consists in a catalytic decomposition of the hydrogen peroxide. In the case of very dilute gaseous mixtures the reaction of this compound is seen to be similar to that of ozone, thus preventing a distinction by means of potassium iodide.

However, a distinction between these two gases can always be made qualitatively by means of a solution of titanium sulphate in sulphuric acid. This solution becomes yellow in presence of very small quantities of hydrogen peroxide, but is unaffected by ozone.

Summary of Results.

The reactions of potassium iodide with ozone, hydrogen peroxide, and nitrogen peroxide show the following characteristics. With ozone the ratio of the different products is a function of the concentration of the gas and of the total amount passed. With a very dilute gas no iodate is formed, but only hypoiodite and free iodine, and no potassium hydrate.

However, at temperatures below -24°, the cryoscopic point of the reagent, this relation does not hold.

With nitrogen peroxide the reaction results mainly in the formation of iodate, whatever the dilution of the gas. In presence of an acid solution of potassium iodide, nitrogen peroxide even when present in minute quantities shows the property of continuously liberating iodine from the reagent when in presence of air. This reaction forms a distinguishing and very delicate test for this gas.

Hydrogen peroxide, at high dilutions, reacts with potassium iodide similarly to ozone. However, a definite distinction can be made between these gases by means of titanic acid.

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THE MECHANISM OF ANODIC REACTIONS AND THE BEHAVIOUR OF IRON AND NICKEL ANODES.*

By E. P. SCHOCH,
Professor of Chemistry in the University of Texas.

NERNST'S solution tension theory assumes essentially that metal particles separate from the mass of the metal and enter the liquid direct as ions. This notion was formed from the thermodynamic expression for the electrode potential, and as thermodynamic relations are entirely independent of the "paths" through which the transformations take place, we should not be surprised to find that a study of the details of the action leads us to assume an entirely different mechanism for the electrode changes, particularly in order to harmonise our conception with our present knowledge of the properties of electrons,

The existence of free electrons in metals makes it logical and permissible to assume that when a metal is in contact with an electrolyte, electrons enter the solution and neutralise the charges on the cations in the immediate vicinity. The difference of potential thus set up between the liquid and the metal draws the anions to the latter, and on contact they react with the metal right on the surface of the latter. The resulting compounds, if soluble, then enter the solution. Similarly, the action at a cathode, during electrolysis, consists of the projection of electrons *into* the electrolyte and the neutralisation by these electrons of cations near the cathode. The neutralisation takes place away from the cathode, and the separation of the neutral metals from the electrolyte and their deposition on the cathode is a subsequent change.

There are many facts that support the view that the neutralisation of cations takes place *within* the electrolyte; we need but recall the fact that the passage of the current is hindered but slightly by gas films such as are found on metals which exhibit the phenomenon of over-voltage, and that the passage of the current is hindered but slightly by films which cover the surface of the aluminium in the electrolytic rectifier when the aluminium acts as the cathode. Again, the neutralisation of the electric charges on cations while the latter are still within the liquid is indicated by the co-deposition of metals in the form of alloys, and by the observation of supersaturated *neutral metal* solutions in connection with their electrodeposition (*Zeit. Elektrochem.*, xiii., 1477; *Trans. Chem. Soc.*, 1907, 385; *Abh. Bunsen Ges.*, No. 3, p. 75). In the latter instance, electric discharge does not necessarily take place "at a distance" from the cathode, but in the first-mentioned instance above, gas films certainly prevent direct contact between cations and cathode. That the passage of electrons from cathode to electrolyte through gas films actually takes place *readily* during electrolysis has been positively established by Guenther Schulze in his study of electrolytic rectifiers (*Ann. d. Phys.*, xxi., 929; xxii., 543; xxiii., 226; xxiv., 43; xxv., 775; xxvi., 372; xxviii., 787; and still later papers).

This modification of Nernst's original conception of cathode actions follows as a matter of course from our present knowledge of electrons and the immobility of positive electric charges. However, this does not compel any modification of Nernst's view applied to the anodic dissolution of metals; and it is probably on this account that the notion of the direct formation of cations from metals is still adhered to more or less definitely. Even Le Blanc (see Note), who was the first to point out that all electrode reactions take place with a finite velocity and hence involve chemical changes besides the electrical change, considered that "the usual conception of the primary formation of the metal ions" is able to account for this finite velocity if it is amplified by the idea that the *primary* cations undergo the chemical change of hydration before they are in their final form.

(NOTE.—M. Le Blanc, "Die Elektromotorischen Kraefte der Polarisation, und Ihre Messung mit Hilfe des Oszillographen," *Abh. Bunsen Ges.*, No. 3; see also Reichinstein, *Zeit. Elektrochem.*, 1910, xvi., 916, who observed polarisation even in those cases in which Le Blanc observed none definitely).

However, in this same publication Le Blanc states that the idea of a direct attack of the anions upon the metal anodes may also be assumed to be the course of the reaction, this chemical change determining the finite velocity. He states that at the time of the writing of that article (March, 1909) both mechanisms of anodic reaction must be admitted as equally possible, and he suggests that they may take place simultaneously, and that the conditions may make one or the other more prominent. However, he does not mention the direct "anion-metal" reaction beyond this general statement.

The notion of the direct formation of cations from metals has the vital defect of not taking into account, in any direct manner, the well-known specific effect of the particular anions present. For a striking illustration of the latter effect one need but point to the difference in the rate of the action of zinc with dilute sulphuric acid and with dilute hydrochloric acid; or to the marked effect of the small amounts of certain anions such as the chloration, added to sulphuric action in the Planté method of forming positive storage-cell plates. This specific effect of the anions is best accounted for by assuming a direct attack of the solid metal by the anion with the subsequen dissolution of the compound.

As the facts appear to the writer there is nothing in the behaviour of metal anodes that requires the assumption of the direct formation of cations from metals in contradistinction to the direct attack of the anode by the anions, and since the latter mechanism of the reaction must actually be assumed to take place in many cases, only this mechanism of the reaction will be considered in the remainder of the article.

This conception of anode changes takes care of the specific influence of the anions, and leads us to expect that the velocity of reaction depends upon *both* reacting components; but before the general behaviour of anodes can be considered some other facts must be taken into account.

Guenther Schulze (*Ann. d. Phys.*, xxviii., 789) has shown that in the electrolysis of phosphate, borate, &c., solutions with an aluminium anode, the following distinct layers are formed upon the metals:—First, a very thin, non-porous layer of oxide; second, a porous layer of oxide which becomes thicker with increasing potential,

* A Contribution to the General Discussion on "The Passivity of Metals," held before the Faraday Society, November 12, 1913.

and which is slowly but constantly reformed next to the metal as the layer next to the electrolyte is slowly dissolved; third, oxygen gas, which fills the pores of the porous film. He also observed an evolution of oxygen gas on the surface between the film and the electrolyte. His conclusions concerning the formation of these films are the following:—

1. The first, very thin, film of oxide on the metal is formed by the oxygen of the air.

2. This thin layer hinders or prevents direct access to the metal of complex anions such as sulphation, phosphation, &c., and under the stress of the potential drop through this layer, these anions dissociate, producing an equivalent number of oxygen ions which on account of their lesser bulk can pass through the oxide layer (and in passing through it perforate it) and then reach the metal surface to be discharged there. The oxygen discharged on aluminium naturally forms a new layer of aluminium oxide next to the metal, while the outer portion of this oxide layer, made porous by the passage of the oxygen ions, develops the porous layer.

3. As the oxide layer thickens, the potential fall in it becomes great enough for some of the ions to give up their electrons before they reach the electrode, thus forming oxygen gas: the passage of the free electrons through the dielectric is plainly shown by numerous fine sparks.

It is needless to follow Schulze's explanation beyond this point, because his other observations have no bearing on the question of ordinary anode actions. The following general conclusion may be drawn from his work and should be emphasised:—A film, or cover, over the surface of an anode will hinder or prevent the direct access to the surface of the metal of complex anions and will bring about the formation of oxygen ions from them. The latter pass on to be discharged on the surface of the metal.

This gives us all the facts necessary for the explanation of the chemical change of any anode in any electrolyte. Briefly this explanation may be stated as follows:—With a clean anode surface the anions come in direct contact with the metal, react with it, and give up their electrons: the rapidity of the reaction and the final products obtained will vary greatly with different metals and different anions. The product may be so rapidly formed and so rapidly dissolved that other anions may have unhindered access to the surface. Again, the reaction may take place slowly, or the product may dissolve slowly, or the latter may be insoluble, or it may be hydrolysed into an insoluble compound, so that other ions may find their progress to the anode more or less obstructed—a condition that may naturally be brought about in almost any case by a sufficiently great current density. Many complex ions which are prevented by the obstruction from reaching the surface of the metal will dissociate into an equivalent number of oxygen ions, which reach the surface of the metal more readily. Upon discharge these oxygen ions may form the oxide of a metal (as with copper in sulphate electrolytes), or they may form partly an oxide and partly oxygen (as with platinum in sulphate electrolytes), or they may react so slowly that the discharged oxygen still in contact with the metal becomes gradually more condensed as more oxygen ions are forced into the same area with a greater potential difference until finally gaseous oxygen, or perhaps some higher oxide of the metal, is formed.

(To be continued).

Iron and Steel Institute.—The Annual Meeting will be held, by kind permission, at the Institution of Civil Engineers, Great George Street, Westminster, on Thursday and Friday, May 7 and 8, 1914. The Bessemer Gold Medal will be awarded to Mr. Edward Riley, F.C.S. The Annual Dinner will be held in the Connaught Rooms, Great Queen Street, W.C., on Thursday, May 7, 1914. The Autumn Meeting will be held at Paris, on September 18 to 23, 1914, by the kind invitation of the Comité des Forges de France.

THE SCIENTIFIC WEEK.

(From Our Own Paris Correspondent).

The Rôle of Fluorine in Animals.

For more than a century past the existence of fluorine had been known in the teeth and bones. Taking up these researches with M. Clausmann, M. Armand Gautier established in 1912 that fluorine is spread through all the organs of animals, but in very different proportions. There are 190 mgrms. in the enamel of the teeth and 0·750 mgrm. in the muscles. What is the rôle of this very active substance? MM. Gautier and Clausmann have established the fact that fluorine accompanies phosphorus everywhere, without however being proportional to it. Analyses made of the white and yellow of egg, of different milks, of the blood of carnivorous animals and herbivorous animals show that fluorine and phosphorus increase and decrease together. In the noble tissues of intense life, the brain, liver, pancreas, it is found that one part of fluorine suffices to bind 450 to 750 parts of phosphorus. In the hard tissues of life—bones, cartilages—one part of fluorine binds on an average only 150 times its weight of phosphorus. In the tissues of products of excretion, products of mechanical defence, or of ornamentation, such as hair, nails, feathers, epidermis, the fluorine no longer retains more than 3·5 or seven parts of phosphorus. Henceforth having become unfit for life, the fluorine is thrown off by the fall of the hair, down, or epidermis. Thus the accumulation of fluorine in these products, which in themselves are not inherent to life and are destined to be thrown out.

A Gigantic Electro-Magnet.

For some time past physicists have been seeking to realise extremely powerful electro magnets so as to be able to examine the intimate construction of matter. Already Prof. Jean Becquerel had succeeded in having an electro-magnet constructed of a magnetic power of 50,000 gauss. This apparatus, weighing more than 1100 kilogrms., lately installed in the cellars of his laboratory, has not yet been experimented with. Recently the Academy of Sciences had a very interesting communication from M. Deslandres, the learned director of the Observatory of Meudon, who, in his own name and in that of Prof. Perot, has shown two models of electro-magnets enabling powerful fields to be obtained with apparatus of low weight. The different pieces of the unmounted electro-magnet very much interested the members of the Institute. The apparatus does not weigh more than 30 kilogrms., and at its full force, 50,000 gauss was reached and even exceeded. The characteristic of these electro-magnets is the employment, as conductors, of thin copper bands, furnished with a system for cooling with petroleum, carried to 30° below zero. It is well known how much interest is attached to these researches on account of the importance of magnetic effects on the emission and absorption of light. In astronomy the study of emitted light has enabled important magnetic fields to be recognised on the surface of the sun. M. Appel, president of the learned assembly, commented on this interesting communication, and suggested the idea of the construction of a much more powerful electro-magnet, destined to be used in the Sorbonne and in a cold laboratory for the study of very low temperatures analogous to the laboratory of Prof. Kamerlingh Onnes at Leyden. This double erection would contribute to found a centre of scientific studies that does not at present exist in Paris.

The Installisation of Prof. Charles Richet.

Prof. Charles Richet, elected a week ago titulary member of the Academy of Sciences in the section of medicine and surgery, was present at this week's sitting of the Academy. The President, M. Paul Appel, Dean of the Faculty of Science, at the opening of the meeting, welcomed the eminent physiologist, and invited him to take his place among his colleagues.

EULOGY OF SIR DAVID GILL.

M. Appel mentions the death of the learned English astronomer, Sir David Gill, correspondent of the French Academy of Sciences since 1896, and a great friend of France.

A NOTICE ON M. RADAN.

According to academical tradition, which requires that each newly elected member shall make the historical praise of his predecessor and which is now adopted by the Academy of Sciences, M. Pierre Puiseux, astronomer of the Paris Observatory, reads a paper on the life and works of M. Radan, eminent astronomer and delicate writer, who died a little over two years ago, and who is succeeded by M. Puiseux.

CURIOUS ANALOGIES BETWEEN INSECTS AND CRUSTACEÆ.

Insects and crustaceæ being animals belonging to two different classes have, generally, organs that are very differently constituted. In a study presented by M. Henneguy, M. Lecaillon, Professor at the Faculty of Science of Toulouse, shows that certain insects, the collemboles, have nevertheless an ovary, the construction of which resembles that of the ovary of a little crustacean, the chirocephalopod. The fact is interesting from a biogeological point of view, and particularly from a phylogenical point of view.

A MERCURY ARC WITH ALTERNATE CURRENT.

Two young physicists, M. Maurice Leblanc, jun., and M. Darmois, have just, for the first time, succeeded in realising a mercury arc with alternate current. In their work, communicated by Prof. Boity, they mention that with this arc, for a luminous intensity of 3000 candles, the consumption does not exceed 0·21 watt per candle. It is also possible to prime or light an arc even when there is an empty space between the electrodes.

THE INFLUENCE OF TEMPERATURE ON ASTRONOMICAL OBSERVATIONS.

In astronomy many measures of precision are taken by means of micrometric screws, worked up with the greatest care, so that all the threads are exactly equal, but the angular value of the thread is modified by the variations of temperature. The determination of this influence of the temperature is a long and delicate operation. M. Bigourdan has indicated a simple process to arrive at this result, by utilising a method recently explained by M. Lippmann, so as to obtain the veritable focal distance of an objective by autocollimation.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, January 29th, 1914.

SIR WILLIAM CROOKES, O.M., President, in the Chair.

PAPERS were read as follows:—

"*Origin of Thermal Ionisation from Carbon.*" By Prof. O. W. RICHARDSON, F.R.S.

In a paper recently communicated to the Society by Dr. J. N. Pring, experiments bearing on this subject were described. The smallness of the observed currents and the variation of them with the pressure and nature of the gas, led Dr. Pring to the conclusion that considerable doubt was thereby cast on the theory of the emission of electrons from hot solids, and that these effects were to be attributed to chemical action.

In the present paper the magnetic field due to the large heating currents employed by Dr. Pring are shown to curl up the paths of the electrons, and so prevent them from reaching the electrode. It is shown that with the larger currents none of the electrons could reach the electrode in these experiments, and owing to the complexity of the apparatus it is impossible to say what proportion would reach it at the lower temperatures.

It is pointed out that an increase of the observed currents is to be expected on account of—(*a*) the interference of the gas molecules with the motion of the electrons, and (*b*) the combination of electrons with atoms and molecules of the gases.

In the opinion of the author of this paper, the conclusions referred to cannot be regarded as established by the experiments under consideration.

"*The X-ray Spectra given by Crystals of Sulphur and Quartz.*" By Prof. W. H. BRAGG, F.R.S.

A crystal of quartz is found, on examination by the X-ray spectrometer, to contain three interpenetrating hexagonal lattices of silicon atoms and six of oxygen. The angles of reflection in a number of important planes all agree, within 1 or 2 per cent, with the calculated values. Sulphur contains eight interpenetrating lattices, each of the kind formed by placing an atom at each corner of a rectangular parallelopiped and in the centres of two opposite faces. The edges of the parallelopiped are in the known ratios of the crystallographic axes. One element of the movement by which the eight lattices can be successively derived from each other consists of a translation along the "c" axis equal to one-eighth of the length of that axis.

"*Temperature Variation of the Photo-elastic Effect in Strained Glass.*" By Prof. L. N. G. FILON, F.R.S.

The experiments described in this paper were undertaken to see whether the double refraction produced in glass by stress was at all affected by change of temperature.

The apparatus in which the specimens were strained under flexure was enclosed in a copper box with hollow walls, in which steam could be made to circulate freely. The refractive indices were then measured by a method described in *Roy. Soc. Proc.*, A, lxxxiii., 572—579.

The glasses examined were Jena "Uviol" glasses, examined at ordinary temperatures some years previously. These were heated to 90°, and photographic observations of the refractive indices taken. After cooling again to 18° the observations were repeated.

The results show that the refractive indices for rays polarised in and perpendicular to the line of stress are unequally affected, but seem increased on the whole by rise of temperature.

One of these, however, shows a permanent residual change even after cooling. This is important as showing that this property of the glass is affected by previous temperature treatment.

Various irregularities in the graphs of the refractive indices are also discussed.

"*Studies in Brownian Movement.* Paper I. *Brownian Movement of the Spores of Bacteria.*" By J. H. SHAXBY and E. EMRYS ROBERTS, M.D.

"*Transmission of Cathode Rays Through Matter.*" By R. WHIDDINGTON, D.Sc.

"*Variation with Temperature of the Specific Heat of Sodium in the Solid and the Liquid State; also a Determination of its Latent Heat of Fusion.*" By EZER GRIFFITHS.

The specific heat of sodium (melting-point 97·6°) was investigated at various temperatures in the range 0° to 140° by the electrical method. The range of temperature through which the metal was heated was about 1·5°, thus enabling the actual specific heat at each particular temperature to be determined.

In the solid state the specific heat is considerably influenced by the nature of the previous heat treatment, and two distinct specific heat temperature curves are obtained for the annealed and the quenched state.

The increase in the values of the specific heat in the solid state is very marked as the melting-point is ap-

proached. The variation may be indicated by the following approximate values of the atomic heat for the annealed state:—

Temperature ..	0°	50°	96°
Atomic heat ..	6·5	6·8	7·5

In the molten state the specific heat decreases with temperature, the relation between specific heat and temperature from 100° to 140° being linear. The latent heat of fusion was found to be 27·52 grm. calories.

"*Natural Radiation from a Gas.*" By George Green, D.Sc.

The investigations of Planck have established the result that the total energy emitted from a black body at any temperature consists of discrete quanta, all equal and similar. This does not necessarily imply that energy has an atomic structure. It may arise from the nature of the radiating molecules, which may be such that emission of energy takes place accompanied by some definite change within the molecule, such as the expulsion of an electron or the rearrangement of the system in a new equilibrium condition. If we identify the "energy quantum" as the energy contained in the light pulse emitted each time a molecule undergoes some such structural change, the determination of the form of this light pulse might lead to useful information regarding the constitution of the molecule.

In this paper the form of pulse, in which the energy per wave-length is the same as that required by Planck's Law of Radiation at any temperature, is first derived. This form accordingly represents the total radiation from any black body at any temperature. The radiating body is now taken to be a gas. By decomposing the above pulse we obtain an infinite succession of wave-trains emitted by the various groups of molecules obtained by arranging the total number according to speed.

"*Similarity of Motion in Relation to the Surface Friction of Fluids.*" By Dr. T. E. Stanton and J. R. Pannell.

The paper deals with an experimental investigation of the existence of the similarity of motion in fluids, of widely differing viscosities and densities, in motion relative to geometrically similar surfaces, which has been predicted from considerations of dynamical similarity by Stokes, Helmholtz, Osborne Reynolds, and Lord Rayleigh. The theory in its most general form may be expressed by the relation—

$$R = \rho v^2 f\left(\frac{v.L}{\nu}\right)$$

where R is the resistance per unit area of the surface, ρ density of the fluid, v velocity, L a linear dimension of the surface, ν kinematical coefficient of viscosity of the fluid, and the assumptions made in the derivation of the expression are that R depends solely on ρ, L, v, and ν.

The method of experimentally demonstrating the sufficiency of these assumptions has been by a determination of the surface friction of air and water flowing through smooth pipes of varying diameters and with as great ranges in velocity as possible, and so obtaining values of the condition for similarity of motion, which is that for the same values of $v.d/\nu$ in either fluid the values of $R/\rho v^2$ should be identical.

The experiments show that this condition is fulfilled with considerable accuracy through a range in the value of $v.d/\nu$ of from 2500 to 430,000. To obtain this range with the comparatively small diameters of pipes used, mean velocities of flow up to 6000 centimetres per second have been reached.

From these data it has been possible to investigate the limits of accuracy of the well-known Index Law of the Resistance of Fluids, $R = kv^n$, and by a determination of the value of n at different points of the range of velocity it appears that n is not constant for any particular surface but gradually increases as the value of $v.d/\nu$ increases. In this way gradual variations in the value of n from 1·72 to 1·92 have been detected.

"*Influence of Molecular Constitution and Temperature on Magnetic Susceptibility.*" By A. E. Oxley.

"*Boiling-point of Sulphur on the Thermodynamic Scale.*" By N. Eumorfopoulos.

CHEMICAL SOCIETY.

Ordinary Meeting, January 22, 1914.

Prof. W. H. Perkin, LL.D., F.R.S., President, in the Chair.

The President referred to the loss sustained by the Society, through death, of William Popplewell Bloxam and John Gibson.

It was announced that the Council desired to draw the attention of Fellows to the fact that the Faraday Society is prepared to consider the election to membership of a certain number of Fellows of the Chemical Society without the usual entrance fee.

Certificates were read for the first time in favour of Messrs. Sydney Edward Davenport, Fernbank, York Road, Windsor; Charles George Fernie, B.Sc., Holmleigh, Northwood, Middlesex; George Ingle Finch, 41, Ladbroke Road, W.; Reginald Furness, M.Sc., 90, Woodlands Road, Ansdell, Lytham; Gopal Balkrishn Kolhatker, M.A., Ferguson College, Poona, India; Frederic William Leighton, Lydiard Tregoze, Wootton Bassett, Swindon; Rowland Ernest Oldroyd, 90, Park Road, Rochdale; William Henry Pick, B.Sc., 141, Mare Street, Hackney, N.E.; Frederick Alfred Pickworth, 70, Highfield Road, Dartford; Conly Hunter Riley, Anchorage, Clayton-le-Moors, Accrington; Joseph de Carle Smith, B.Sc., Oak House, Newmarket Road, Norwich; Horace Gilbert Stone, B.Sc., 24, High Street, High Wycombe.

A certificate has been authorised by the Council for presentation to ballot under By-law I. (3) in favour of Mr. Lionel Cohen, Stock Department Laboratory, Casino, N.S.W.

Of the following papers, those marked * were read:—

*1. "*Crystals of Organic Compounds Coloured Blue by Iodine.*" By George Barger and Walter William Starling.

In a previous paper (Barger and Field, *Trans.*, 1912, ci., 1396) it was pointed out that the blue compounds formed from various organic substances and iodine may be either amorphous or crystalline; the former cases are typical examples of adsorption. The blue crystals may be regarded as solid solutions of iodine in the organic substance, in proportions not necessarily stoichiometric. They only result when the crystal is formed in the presence of iodine, either from a solution containing iodine, or by sublimation in the presence of iodine (compare for analogous cases Bruni, "Feste Lösungen und Isomorphismus," 1908, p. 95). Colourless crystals of the organic substance, when once formed, cannot be made to take up iodine. In most of the cases studied so far, the blue crystals have been obtained from solutions in mixtures of water with an organic solvent, but this need not be the case always; narceine, for instance, when dissolved, together with iodine, in pyridine, gives rise to blue crystals on adding light petroleum. All the blue crystals examined so far are more or less strongly pleochroic; no connection has been detected between the crystalline form and the capacity for yielding "mixed" crystals with iodine.

Discussion.

In reply to the President, Dr. Barger expressed the opinion that the additive compounds described might be analogous to oxonium compounds, but since they were also given by substances not containing a pyrone nucleus, they might possibly show greater analogy to the potassium additive compounds of ketones, described by Schlenk and Thal (*Ber.*, 1913, xlvi., 2840). No analogous bromine compounds had been observed.

*2. "*The Mutual Solubility of Formic Acid and Benzene, and the System: Benzene-Formic Acid—Water.*" By ARTHUR JAMES EWINS.

Formic acid was found to be partly miscible with a number of organic liquids. The mutual solubility of formic acid with benzene was studied in detail.

The critical solution temperature (maximal) of these two liquids affords a very sensitive means of determining the purity of the components, and was therefore employed for this purpose. For the purification of formic acid, fractional distillation was employed, followed by careful fractional crystallisation, until the critical solution temperature with pure benzene remained constant (73·2°).

The acid so obtained melted at 8·39°, boiled at 100·47°/760 mm., and had $D^{18}/_4$ 1·2259. The acid showed very little supercooling on freezing, the actual figures in three determinations being 0·40°, 0·15°, and 0·35°.

Benzene was purified by fractional crystallisation and distillation from sodium. The melting-point was found to be 5·57°. The ternary system benzene-formic acid-water was also studied.

*3. "*The Condensation of Ethyl Glutaconate.*" By RAYMOND CURTIS and JAMES KENNER.

The condensation products isolated by Blaise (*Comptes Rendus*, 1903, cxxxvi., 639) and by von Pechmann (*Ber.*, 1904, xxxvii., 2113) from the action of sodium ethoxide on glutaconic ester were shown to be identical, and a probable constitution was assigned to them. Certain discrepancies between the accounts given by the two investigators named were also examined.

α-Ethylglutaconic ester, after treatment with sodium ethoxide in the same manner as glutaconic ester, was recovered unchanged.

DISCUSSION.

Prof. J. F. THORPE stated that his experience with the behaviour of ethyl glutaconate on alkylation led him to think that the action of ethylene dibromide on this substance would most likely yield a derivative of *cyclo*pentane, and not the *cyclo*propane derivative suggested by Dr. Kenner. It would be of great interest to apply this reaction to the case of ethyl β-methylglutaconate, the two forms of which were sufficiently stable to withstand ordinary experimental conditions.

Dr. KENNER, in reply, pointed out that Fecht had proved one of the products of the condensation of ethyl glutaconate with ethylene dibromide to be a *cyclo*propane derivative by the identity of its reduction products with a synthetic acid of known constitution.

*4. "*2 Hydrindamine.*" By JAMES KENNER and ANNIE MOORE MATHEWS.

The preparation of 2-hydrindamine from ethyl hydrindene-2-carboxylate by Curtius's method was described, and the base was characterised by means of a number of derivatives.

*5. "*An Attempt to Prepare Organometallic Derivatives of Tungsten.*" By EUSTACE EBENEZER TURNER.

It was shown that tungsten, in common with all elements situated in even series or in sub-group A of the periodic classification, cannot be converted into organometallic compounds by means of the Grignard reagent. The higher chlorides of tungsten are, instead, reduced, the chlorine removed decomposing the Grignard reagent to produce a mixed magnesium haloid salt and a hydrocarbon consisting of the two diaryl residues linked together, according to the general equation—

$$WCl_x + xRMgX = \\ = WCl_{x-2} + 2ClMgX + (x-2)RMgX + R{\cdot}R.$$

*6. "*The Absorption Spectra of Nitrated Phenylhydrazones.*" By JOHN THEODORE HEWITT, RHODA MARIANNE JOHNSON, and FRANK GEORGE POPE.

The absorption spectra of the *p*-nitrophenylhydrazones of benzaldehyde and acetophenone have been measured. Addition of alkali to the alcoholic solutions leads to salt-formation, accompanied by considerable change in the absorption spectra. The absorption of the two hydrazones mentioned is very similar to that of *p*-nitrobenzaldehyde-phenylhydrazone, although when the latter compound is acetylated, the absorption experiences a strong displacement towards the ultra-violet.

7. "*Unstable Compounds of Cholesterol with Barium Methoxide.*" By EDGAR NEWBERY.

Barium oxide in presence of excess of methyl alcohol forms an unstable solid compound with cholesterol, which is dissociated in organic solvents, such as ether, benzene, &c., to an extent depending on the temperature and also on the concentration of the excess of methyl alcohol present, a state of equilibrium being set up between the cholesterol in the solid and that in the liquid. This state of equilibrium is attained much more rapidly when the compound is being decomposed than when it is forming. The compound is readily decomposed by water, carbon dioxide, or acetic acid. Hexadecyl alcohol shows a similar behaviour to cholesterol.

A knowledge of the above reactions is of importance when attempting to extract cholesterol and cerebrones by Smith and Mair's method (*Journ. Path. Bact.*, 1910, xv., 122).

8. "*A Study of the Vapour Pressure of Nitrogen Peroxide.*" By ALFRED CHARLES GLYN EGERTON.

Following some work on the vapour pressure of bromine, and in connection with the measurement of small quantities of nitrogen peroxide, the vapour pressure of solid nitrogen peroxide has been investigated down to as low a temperature as −100°. The method employed in these measurements consisted in the saturation of a known volume of hydrogen, as it passed over the nitrogen peroxide, and the estimation of the amount of the latter carried over.

The measurements follow a certain curve which has a somewhat steeper slope than other measurements would appear to indicate, although these have not, so far, been carried below −35°. The vapour pressure curve of nitrogen peroxide was discussed, and, with the aid of Nernst's vapour pressure equation, approximate values of some of its chemical and physical constants were derived.

9. "*Organic Derivatives of Silicon. Part XXI. The so-called Siliconic Acids.*" By ARTHUR JAMES MEADS and FREDERIC STANLEY KIPPING.

Many compounds supposed to have the structure $R{\cdot}SiO{\cdot}OH$ and to represent the silicon analogues of the carboxylic acids have been described in the literature. The first case was that of silicopropionic acid, $EtSiO_2H$ (Friedel and Ladenburg); shortly afterwards silicoacetic acid, $Me{\cdot}SiO_2H$, silicobenzoic acid, $Ph{\cdot}SiO_2H$, and silicotoluic acid, $C_6H_4Me{\cdot}SiO_2H$, were described by Ladenburg (*Ann.*, 1875, clxxix., 143). In more recent times many other aliphatic and aromatic siliconic acids have been prepared by Khotinsky and Seregenkoff (*Ber.*, 1908, xli., 2946), and by Melzer (*Ber.*, 1908, xli., 3390).

Now the results of the study of the diarylsilicanediols, $R_2Si(OH)_2$ (Kipping, *Trans.*, 1912, ci., 2108, 2125; Robison and Kipping, *Ibid.*, 2142, 2156), seemed to indicate that compounds of the type $RSi(OH)_3$ would not pass into siliconic acids, $R{\cdot}SiO_2H$, by loss of the elements of water, but would give gise to a series of condensation products, probably analogous to those of the diarylsilicanediols. An exhaustive examination of the so-called silicobenzoic acid has gone far to establish this view; the product of the hydrolysis of phenylsilicon trichloride is not one compound of the composition $C_6H_5{\cdot}SiO_2H$, but a complex mixture of condensation products, primarily derived from the trihydroxy-derivative, $C_6H_5{\cdot}Si(OH)_3$. It is very probable, therefore, that all the so-called siliconic acids are merely mixtures; the experiments are being continued in order to test this inference.

10. "*The Reactions of* iso*Amarine.*" By HENRY LLOYD SNAPE.

*iso*Amarine and methyl iodide react at the ordinary tem-

perature, when benzene is employed as a solvent, with the production of the *methiodide*, $(C_{21}H_{18}N_2)_2,CH_3I$, which, on crystallisation from benzene, melts at 135°.

By the action of acetyl chloride on a solution of *iso*amarine in ethyl acetate or chloroform and heating the product with absolute alcohol, a crystalline substance, melting at 235—236°, was obtained, which proved to be an isomeride of the compound called "diacetylamarine" by Bahrmann, but shown by Japp and Moir (*Trans.*, 1900, lxxvii., 636) to be acetylbenzoyldiphenylethylenediamine, $C_{23}N_{22}O_2N_2$, which melts at 316°). The six-sided plates mentioned in a former paper (*Trans.*, 1900, lxxvii., 780) as having been obtained in small quantity as the result of the action of acetyl chloride on *iso*amarine followed by treatment with alcohol, proved to be *iso*amarine hydrochloride.

When *iso*amarine, dissolved in a very small quantity of glacial acetic acid, was treated with fuming nitric acid, a *mononitro*-derivative was obtained, which melted at 82—85°. Fuming nitric acid at 60° acted on *iso*amarine, forming a *dinitro* derivative, which melted at 175—176°.

The values previously published for the rotation of *d*- and *l*-*iso*amarine and of the corresponding tartrates have been corrected.

Sulphates of *d*- and *l*-*iso*amarine were described. The former has the formula $(C_{21}H_{18}N_2)_2,H_2SO_4$, melts at 266—267°, and its rotatory power, $[\alpha]_D$, is +151·1° to +155·7°. The corresponding particulars with respect to the lævo-salt are $(C_{21}H_{18}N_2)_2,H_2SO_4,\frac{1}{2}H_2O$, 280—285°, and −144·1°. On addition of nitrosyl sulphate to *d*-*iso*amarine sulphate, a white crystalline substance is precipitated which has the composition $(C_{21}H_{18}N_2)_2,H(NO)SO_4,\frac{1}{2}H_2O$.

11. "*The Constituents of* Solanum angustifolium: *Isolation of a New Gluco-alkaloid, Solangustine.*" By Frank Tutin and Hubert William Bentley Clewer.

The material employed in this investigation consisted of the leaves, twigs, and flowers of *Solanum angustifolium*, Ruiz et Pavon.

For the purpose of a complete examination, 30·92 kilogrms. of the dried and ground material were completely extracted with hot alcohol, and the resulting extract distilled with steam.

From the portion of the extract which was soluble in water, there were isolated the following substances:—(i.) Quercetin; (ii.) rutin; (iii.) *l*-asparagine; (iv.) a new gluco-alkaloid, *solangustine*, $C_{33}H_{53}O_7N,H_2O$. The aqueous liquid also contained small amounts of an amorphous alkaloid and a considerable quantity of sugar, together with amorphous viscid products which, on hydrolysis, yielded quercetin and 3:4-dihydroxycinnamic acid.

The portion of the extract which was insoluble in water yielded the following definite substances:—(i.) Triacontane; (ii.) a phytosterol, $C_{27}H_{46}O$; (iii.) a phytosterolin (phytosterol glucoside), $C_{33}H_{56}O_6$; (iv.) palmitic, stearic, cluytinic, and cerotic acids, together with a mixture of linolic and linolenic acids.

The *hydrochloride*, *nitrate*, and *sulphate* of solangustine are insoluble in water and most organic solvents. The last mentioned salt forms colourless needles, and has the formula $(C_{33}H_{53}O_7N)_2H_2SO_4,3H_2O$.

On hydrolysis with dilute acid, solangustine yields *solangustidine*, $C_{27}H_{43}O_2N$, and dextrose—

$$C_{33}H_{53}O_7N + H_2O = C_{27}H_{43}O_2N + C_6H_{12}O_6.$$

Solangustidine is amorphous, but a crystalline *hydrochloride*, *hydrobromide*, *nitrate*, *sulphate*, *picrate*, and *acetyl* derivatives have been prepared from it.

The entire alcoholic extract of the plant, the new gluco-alkaloid, solangustine, and the amorphous alkaloidal material were separately administered to a dog, but produced no appreciable physiological effect.

12. "*Studies of the Constitution of Soap Solutions: Electrical Conductivity of Potassium Salts of Fatty Acids.*" By Hugh Mills Bunbury and Herbert Ernest Martin.

The conductivities of the potassium salts (soft soaps) of the saturated fatty acids of even number of carbon atoms from the stearate to the acetate have been measured at 90° by the somewhat laborious method previously described by McBain and Taylor.

The conductivities of the potassium soaps are higher than those of the corresponding sodium soaps, but there is a general resemblance between the form and position of corresponding curves. Closer comparison shows an even greater tendency towards abnormality on the part of the potassium salts; this is not due to the potassium ion as such, for well-developed maxima and minima in the conductivity curves are exhibited from the stearate as far down as the laurate (C_{12}).

The appearance, washing power, density, and conductivity curve of potassium hexoate (C_6) distinctly mark the beginning of that deviation from the behaviour of the acetate, which rapidly and regularly increases through the other members of the homologous series until it attains the typical character of the higher soaps.

In all cases where it is directly visible, the depression in the conductivity curve occurs in the same region of concentration, independent of the nature of the acid or alkali taken. Further investigation may, however, show that the real abnormality is shifted in the case of the lowest homologues to regions of higher concentration.

13. "*The System: Ethyl Ether—Water—Potassium Iodide—Mercuric Iodide. Part I. The Underlying Three-component Systems.*" By Alfred Charles Dunningham.

The System: Potassium Iodide—Mercuric Iodide—Water.—This system has been studied at 20° and 30°. In both cases the following phases are stable in equilibrium with solution:—KI, $KHgI_3$, $KHgI_3,H_2O$, HgI_2.

The System: Potassium Iodide—Water—Ethyl Ether.—Ether and water are only miscible to a small extent, and this is not materially increased by the addition of potassium iodide. Consequently it is possible to obtain:—(1) A small range of homogeneous aqueous solutions in equilibrium with potassium iodide, (2) a small range of homogeneous ethereal solutions in equilibrium with potassium iodide, (3) one pair of invariant aqueous and ethereal solutions in equilibrium with one another and with potassium iodide, and (4) a wide range of conjugate aqueous and ethereal solutions in equilibrium with one another.

The System: Potassium Iodide—Mercuric Iodide—Ethyl Ether.—The following phases are stable in equilibrium with solution:—KI—$KHgI_3$—HgI_2. Under certain conditions a heavy liquid layer separates, rich in dissolved salts, and an equilibrium diagram has been constructed in which the saturation curves of potassium mercuri-iodide and mercuric iodide are cut by a binodal curve, so that each is divided into two portions, separated by a region in which all mixtures exist as two liquid layers.

The System: Mercuric Iodide—Water—Ethyl Ether.—Mercuric iodide is almost insoluble in water and ether, and all mixtures of these two components. The equilibrium is of the same type as that in the system: potassium iodide—water—ethyl ether.

14. "*The Inversion of Sucrose by Acids in Water-alcohol Solutions.*" By George Joseph Burrows.

The rate of inversion of sucrose by acids in water-ethyl alcohol mixtures decreases with increasing concentration of alcohol up to 45 to 50 per cent, and then increases. The catalysis in such a series of solvents is therefore not proportional merely to the concentration of hydrogen ions. The catalytic activity of an acid is affected by the viscosity of the solution, and the influence of the latter is probably the same as in conductivity. If therefore the rates of inversion are divided by the conductivities of the acid in the different solvents, the numbers so obtained represent the relative catalytic activities of the acid. In this way it was found that the replacement of water by alcohol increases the catalytic activity of hydrochloric acid.

In the inversion of sucrose by acids, therefore, the

addition of water may be regarded as decreasing the catalytic activity of the hydrogen ions. This agrees with results obtained by other authors for the anti-catalytic effect of the addition of water in esterification and similar catalytic reactions in alcohol.

(To be continued).

PHYSICAL SOCIETY.

Ordinary Meeting, January 23rd, 1914.

Prof. C. H. Lees, F.R.S., Vice-President, in the Chair.

A paper entitled "*Some Characteristic Curves and Sensitiveness Tests of Crystal and Other Detectors,*" was read by Mr. P. R. Coursey.

The paper describes some experiments recently conducted on different types of wireless detectors, which were undertaken with a view to finding out whether any definite relation could be traced between the sensitiveness and characteristic (or, volt-ampère) curves of a detector.

Sample curves for some of the most common detectors are included in the paper and show that in some cases a fairly good agreement exists between the sensitiveness curve of a detector and the second differential of its characteristic, this being most notably the case in the more stable of the crystal detectors, but at the same time it is abundantly evident that the flexure of the characteristic curve cannot be the only cause of the response of a detector to wireless signals, but that at least a second action must also be present, as in some cases—notably the electrolytic detector—it was observed that the maximum ordinates on the second differential, *i.e.*, the point of greatest change of flexure of the characteristic curve, were at places where the measured sensitiveness was either zero or extremely small, showing that there are probably at least two actions opposing one another at this point. As this is most prominent in the case of the electrolytic detector, it perhaps suggests that this additional action when present in other detectors is electrolytic in nature, or that the received oscillations when superimposed on the direct-current boosting voltage partake of the properties of some "trigger" action (such as in the Zehnder trigger cymoscope). This view is supported by experiments with detectors of the tellurium-aluminium type.

Discussion.

Prof. J. A. Fleming thought it was impossible to avoid speculation in connection with these interesting effects. He thought the real cause of the asymmetry in the case of valve-detectors was the emission of electrons from the hot filament. The laws governing this emission had been shown to be analogous to those governing the evaporation of water. Consequently it could be increased by applying a negative pressure. Some of the irregularities observed might be the equivalent phenomenon to boiling with bumping. He thought it would be of interest if Mr. Coursey's experiments could be repeated at different temperatures.

Mr. W. Duddell thought the investigation was extremely difficult, as one could not be certain that a given pair of crystals would always work in the same way. As far as the crystal detectors were concerned, he did not think the relation between the sensitiveness and the second differential of the characteristic curve was very clear. The determination of the second differential curve was very difficult unless the original observations could be reproduced very accurately.

Dr. W. Eccles thought that the agreement between the characteristic curves given in the paper and those given for the same pairs of substances by previous experimenters showed that the shapes of the curves were undoubtedly dependent on the physical properties of the substances more than on the configuration of the contact. A theory of the cause of the shape of the characteristic curve had been published. The present paper dealt, however, with quite a different matter, namely, the connection between the shape of the curve and the sensitiveness of the detector; the theory of this was also known and was chiefly a matter of geometry.

Mr. D. Owen asked what the measure of sensitiveness adopted by the author was; also if he could furnish figures as to the actual voltage across the contact at limiting silence in the telephone. He would suggest that prediction of the sensitiveness of a particular individual detector might be more simply made from inspection of an *alternating* voltage characteristic—that was, from a graph in which the direct current through the contact under an alternating low-frequency voltage was plotted as ordinate against the alternating volts as abscissa.

Dr. R. S. Willows thought the characteristic curve given for the oscillation valve was not a good one for the purpose. If lower voltages had been used the curve would have possessed three distinct branches. In his experience of the valve, the detector was most sensitive when the voltage was boosted up until it was just at the point of producing ionisation by collision. By making use of the electronic emission from hot lime a better cathode was obtained than in the case of the carbon filament.

Prof. G. W. O. Howe thought too much weight had been attached to slight changes in the characteristics of the crystal detectors. A minute alteration in the point of contact greatly altered the properties of the detector. It would be interesting to hear if Mr. Coursey had repeated his observations. Sometimes a polarising voltage greatly improved the sensitiveness while the slightest shifting of the point might render the polarising voltage quite useless. Since they were so sensitive to slight changes in the conditions, much stress should not be laid on little variations in the characteristic.

Mr. E. H. Rayner thought that some of the irregularities in the characteristics might easily be due to vibration and similar disturbances. He thought it would be useful if the author gave some idea of the resistance of the detectors at maximum sensitiveness, so that one could see if the telephone was doing justice to the detector.

Prof. Fortescue had also found crystal detectors very sensitive to disturbances, such, for example, as the passing of a motor 'bus near the laboratory, and he thought that slight changes from one characteristic to another, rather than real changes in the characteristic, would account for some of the irregularities shown.

The Author, in reply, agreed with Dr. Fleming that it would probably be of great value to conduct experiments similar to those described in the paper at various temperatures, both above and below the ordinary, as in this manner a better insight might be obtained, from the experimental point of view, as to the part played by thermal effects at the contact of the two crystals. The fact that it was unnecessary to have at least one of the contacts of low thermal conductivity was supported by the tests on the tellurium-aluminium detector, in which both materials were metals. These tests seemed to show, however, that the mode of operation of such detectors differed considerably from that of the more ordinary crystal detectors, the type of curves obtained more resembling those of the electrolytic and other detectors in which very little agreement could be traced between the sensitiveness and differential curves. The response of the detector under oscillations seemed in this case to resemble that of a filings coherer, again suggesting something in the nature of a "trigger" action. In reply to Mr. Duddell and Prof. Howe steps were taken in the tests to ascertain to what extent the characteristic curves could be repeated, and it was found that with the "good-contact" detectors, or those operating with moderately firm contact between the crystals, *e.g.*, the "Perikon," almost exact repetition of the curves could be obtained on different occasions, and that although changing the crystals or points of contact altered the scale of the curves, yet in general the main features were present. With the more "imperfect," or "loose-contact," detectors, however, the repetitions were

not nearly so good. The curve shown by Mr. Owen was of interest, but really expressed the response of a detector to signals of various strengths, and did not give the sensitiveness as defined in the paper. In reply to Mr. Rayner, the resistance of the detectors at their points of maximum sensitiveness varied from a few hundred to about 10,000 ohms or more, depending on the crystals used.

Mr. W. Duddell, F.R.S., exhibited a Water Model of the Musical Electric Arc.

In the model the arc is represented by a mushroom valve. The pressure of the valve on its seat is so arranged that the pressure tending to re-seat the valve diminishes very rapidly as the valve lifts. Water is admitted beneath the valve, flows through the valve into the vessel which contains it, and overflows. In order to indicate the difference of pressure on the two sides of the valve which represents the arc a glass pressure column is introduced into the pipe leading to the valve and quite close to it. As the water overflows freely from the tank in which the valve is immersed, the pressure on this side of the valve may be taken as our zero of reference, and consequently the height of the water column in the pressure tube above or below the level of the overflow gives the pressure underneath the valve.

If water be admitted below the valve the pressure in the pressure tube rise to a high value; finally the valve lifts, *i.e.*, the arc is struck, but the pressure still remains high. If, however, the flow of water is increased, the valve will open considerably and the pressure below it will decrease. If nicely adjusted this effect can be made to take place over a considerable range.

If instead of connecting a pressure tube of small bore indicating the pressure on the underneath side of the valve a large diameter tube be introduced so that the water column in it has a periodic time of its own and is able to oscillate similarly to the condenser circuit shunting the arc, oscillations will be set up in this column, and if the periodic time of the liquid in this column be altered, the period of the oscillations will be altered; this can easily be done by connecting air vessels of different capacity to the open end of the tube, so altering the controlling force acting on the water, in other words altering the capacity of the circuit shunting the arc.

With this water model a great many of the properties of arcs both intermittent and oscillating can easily be shown. The one point of difficulty in constructing the model is to obtain a force acting on the valve which decreases rapidly when the valve lifts and which occasions no friction. So far the only successful method which the author has tried is to hang from the underneath side of the valve a piece of soft iron which nearly touches the pole of a small electro-magnet. This gives a force which without any friction rapidly decreases as the valve lifts and works very well.

Mr. C. R. Darling, A.R.C.S., exhibited some "Further Experiments with Liquid Drops and Globules."

The experiments included a demonstration of the structure of a liquid jet by means of orthotoluidine (density slightly greater than 1 at room temperature) issuing from an orifice under water; the formation of spheres of water enclosed in a skin of aniline and of spheres of dimethyl aniline encased in a skin of water; the expansion of a globule of liquid floating on water when a drop of another liquid is allowed to fall on it, and the combination of globules of certain liquids when floating on water. This was well marked in the case of a globule of dimethyl-aniline and a number of smaller globules of orthotoluidine.

A paper entitled "*A Note on Aberration in a Dispersive Medium, and Airy's Experiment,*" by Mr. James Walker, was taken as read.

The view recently adopted by Lord Rayleigh that in the case of aberration we are concerned with the group-velocity instead of with the wave velocity, makes it necessary to consider the experiment of Airy, in which he measured the angle of aberration with a telescope filled with water.

A modification of Lord Rayleigh's explanation of this experiment leads to the result that the angle of aberration thus determined corresponds to an angle $\mu - v/U$ measured in air. The same result is obtained from an analytical investigation, and a numerical calculation shows that the increase in the angle is about 1 per cent—an amount that is probably too small to be detected.

NOTICES OF BOOKS.

Outlines of Theoretical Chemistry. By Frederick H. Getman, Ph.D. (Johns Hopkins). New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1913.

The possession of a working knowledge of elementary physics and chemistry has been presupposed in the students who use this book, although an introductory chapter gives a review of the main principles with which they should be familiar. The theory of electrons is discussed very clearly in an early chapter, which appears in some ways rather out of place, although the reading of it could be postponed until after the chapters on the gas laws, liquids, solids, solutions, &c. Radio-activity is not included, the author believing that the condensed account, which would be all that limitations of space would allow, would not be of sufficient value to justify its insertion. The book is evidently the work of an experienced teacher, and is well written. An error in the diagram illustrating the migration of the ions, which will make the text very difficult to follow by an uninitiated student, will require correction in a second edition.

Quantitative Analysis by Electrolysis. By Alexander Classen, with the Co-operation of H. Cloeren. Translated from the Fifth German Edition by William T. Hall. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1913.

The fifth German Edition of this work has undergone such extensive alteration that for the new English edition practically a fresh translation had to be made. Many advances have been made in quantitative electrolytic work, both in theory and practice, and the author has recently worked out the details of many new rapid methods, which are duly noted in the text. The equipment of the author's laboratory at Aachen is fully described, and directions are given for the estimation and separation of all the more important elements. Some clumsy expressions mar the style of the text; for example, "acts somewhat differently than," "behave similar to." "The current must be kept at 0·35 volts" is evidently a slip.

Second Report to His Majesty's Secretary of State for the Home Department on the Draft Regulations Proposed to be made for the Manufacture of Patent Fuel (Briquettes) with the Addition of Pitch. By Alfred Herbert Lush. London: Darling and Son, Ltd.

This second report on the regulations suggested for adoption in the manufacture of patent fuels (briquettes) with the addition of pitch gives a summary of the former report and an account of the resumption of the enquiry. The action of employers made in response to the circular of November, 1911, is dealt with, and the measures adopted to remedy some defects and to safeguard the health of the employees in some minor respects are described. No definite evidence as to the results of these measures can be adduced. The work of Dr. Ross on the "Origin of Cancer" is described in outline in the report, and the question of the elimination of the injurious constituent in pitch is discussed in some detail. Since the Commissioner recognises that the objects of the issue of the Draft Regulations might be effected more satisfactorily by removing the auxetics and kinetics in pitch than by enforcing the regulations, he finally recommends that they be withdrawn.

Die Atome. ("The Atom"). By JEAN PERRIN. Authorised German Translation by Dr. A. LOTTERMOSER. Dresden and Leipzig: Theodor Steinkopff. 1914. (Mk. 5).

THIS book should be carefully read by all who are interested in modern developments of theories of the constitution of matter and of the nature of the atom. Prof. Perrin's pioneer work in the proof of the actual existence of the molecules is already known to readers of the CHEMICAL NEWS, who will be interested to study in the book further details and the historical development of the problem. The author's aim is broadly "to explain the complicated visible by the simple invisible," and in particular to establish within narrow limits the actual value of Avogadro's constant N, the number of molecules in the grm.-molecule. After a description of the experimental details and an account of the theories underlying the many different methods of arriving at this result, the actual values obtained are tabulated. They show a very remarkable agreement, and the unbiassed reader will find himself bound, whatever prejudices he may have started with, to agree with the author that—"The atomic theory has triumphed, but the atom is no longer to be regarded as an eternal indivisible entity, but as a limitless universe of new worlds, the investigation of which will bring many striking and unforeseen results to light."

Der Heutige Stand der Synthese der Pflanzenalkaloiden. ("The Present Position of the Synthesis of the Plant Alkaloids"). By Dr. HUGO BAUER. Braunschweig: Friedrich Vieweg und Sohn. 1913. (Mk. 4.50).

IN the synthesis of the plant alkaloids problems of very great difficulty have to be solved, and methods hitherto unknown in organic chemistry have had to be worked out for the purpose. This book, which is the fifty-first volume of the "Wissenschaft" series, gives a clear summary of the results which have so far been obtained. The properties and reactions of the alkaloids as a class are first described, and then the methods adopted for the synthesis of individual members of the various groups are given in full. The text is always clear and concise, and workers in this region will find the book a very useful work of reference.

Handbuch der Arbeitsmethoden in der Anorganischen Chemie. ("Handbook of Practical Methods in Inorganic Chemistry"). Vol. III. Part I. Edited by Dr. ARTHUR STÄHLER. Leipzig: Veit and Co. 1913.

THIS volume describes methods of taking physico-chemical measurements, such as the determination of vapour densities, critical constants, specific heats, &c., and includes a lengthy article on metallography. The theory of the methods described is given, as well as full practical details, and no other book rivals it as far as comprehensiveness is concerned. It contains nearly 700 pages and over 350 illustrations, and every large laboratory should possess a copy for reference.

Nouvelles Orientations Scientifiques. ("New Scientific Orientations"). By FERNANDO ALSINA. Translated from the Catalonian by J. PIN Y. SOLER. Paris: Garnier Frères.

ALTHOUGH the author of this book writes temperately and with restraint he makes rather heavy demands upon his reader's faith in his experiments and his deductions from them, when he claims that he has proved that the conceptions of the forces of affinity, cohesion, attraction, polarity, &c., are entirely false. He states that all the phenomena in which such forces are supposed to come into play can be explained by supposing that they are due to the intimate relation between the movements of the ponderable particles of matter and the movements of the ether. The author was encouraged to undertake his researches by Tyndall, and he appears to have given much time and thought to the experimental work which he describes shortly in this book.

Guide pour les Manipulations de Chimie Biologique. ("Guide to Experimental Work in Biological Chemistry"). By GABRIEL BERTRAND and PIERRE THOMAS. Second Edition. Paris: H. Dunod and E. Pinat. 1913.

THIS book contains the details of a large number of practical exercises dealing with the composition of living organisms, diastases, and ferments. Volumetry, microscopic work, and the use of the polarimeter and spectroscope are described, and full directions are given for many qualitative and quantitative experiments with which the student of biological chemistry should be familiar. In the second edition the chapters which have been most largely modified or augmented are those on the acids, alkaloids, proteins, and diastases, and in addition some experiments on the synthetic phenomena brought about by the living organism have been inserted.

Neuere Anschauungen auf dem Gebiete der Anorganischen Chemie. ("New Conceptions in the Realm of Inorganic Chemistry"). By Prof. Dr. A. WERNER. Third Edition. Braunschweig: Frederick Vieweg und Sohn. 1913. (11 Mk.).

A CONSIDERABLE amount of new material has been added to the third edition of this book, which gives a unique survey of the chief theories of inorganic chemistry. The most important additions have been made in the special part which deals with the constitution of inorganic compounds, and which has been very much enlarged by descriptions of recent experimental work. The theories of valency put forward by the author and other workers are lucidly discussed, and the very great advances which have been made during the last five years in our knowledge of the chemistry of complex substances are admirably reviewed.

The Purification of Public Water Supplies. By GEORGE A. JOHNSON. Washington: Government Printing Office. 1913.

THIS bulletin has been written in order to provide officials and citizens with a simple and straightforward statement of the principles and practices governing the purification of waters used for domestic purposes. American methods are principally discussed, but those who are interested in water purification in this country will be able to acquire a good deal of information from the pamphlet. A short historical account of water purification is included, and the method of sterilisation by means of sodium hypochlorite which has been developed in recent years is also discussed. The problems of municipal water softening are shortly treated, and details of the methods of filtration employed in many towns are given.

CORRESPONDENCE.

INSTITUTE OF CHEMISTRY CONFERENCE.

To the Editor of the Chemical News.

SIR,—The letter by Mr. Wilberforce Green in your issue of January 30 comes very near to the most immediately important point for most practising chemists. Professional unity is in any case essential, but we must realise from the outset that the main condition of work of most chemists—namely, whole-time employment by industrial concerns or public departments—are fundamentally different from those of the members of the already recognised professions, such as medicine and law. Just as medical men are already realising, through the British Medical Association, that changing conditions of medical work need altered methods of organisation and professional activity, so chemists must realise now that their special conditions of work involve, if chemists are to take their deserved position in the community, an organisation whose aim and methods shall be specially adapted to those conditions, and not slavishly copied from other professions.

The need of the chemist, the metallurgist, and the physicist is for an Association which aims clearly at the organisation of *all* scientific technologists for the purpose of controlling the conditions of work, the pay, and the methods of entry into the profession, and I am glad to see that Mr. Green, as Secretary of the Association of Chemical Technologists, recognises the need for including "all those who are actively and personally engaged in applied chemistry." Unless chemists determine to work together for this end they will fail both to develop that professional status to which the national importance of their work entitles them, and to obtain such remuneration as will enable them adequately to support that status.—I am, &c.,

RICHARD MATHER.

6, John Street, Adelphi, W.C.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clvii., No. 24, December 15, 1913.

This number contains no chemical matter.

No. 25, December 22, 1913.

Absorption of Ultra-violet Rays by Alkaloids of Morphine Group and by Phenanthrene.—M. Gompel and Victor Henri.—The absorption curve of phenanthrene can be decomposed into three regions, the first of which ($\lambda = 3800—3050$) shows five absorption bands, the second two, and the third one very strong band at $\lambda = 2503$. The absorption curves of morphine and codeine are almost identical, but that of codeine is rather higher than that of morphine. The curve of apomorphine is very much like the phenanthrene curve, and is very different from the morphine curve. The strong phenanthrene band is missing in apomorphine, and hence it is probably due to the double bond between the 9 and 10 carbons, which double bond is saturated in apomorphine.

Catalytic Etherification in the Wet Way.—F. Bodroux.—The power of yielding ether salts in favourable conditions, in presence of an acid catalyst and water, is peculiar to certain monobasic acids of simple function and to primary saturated alcohols of the aliphatic series. The author thinks that most probably an addition product of formula $R.C\begin{cases}OH\\OH\\X\end{cases}$ is formed as an intermediate product, XH being any mineral acid.

Supposed Separation of Radium D from Lead by Grignard's Reaction.—Charles Staehling.—Hofmann and Wölfl have stated that they have effected the separation of radium D from lead in active lead by means of Grignard's reaction. Tetraphenyl lead can be prepared by allowing phenyl magnesium bromide to react with lead chloride, and when active lead was used Hofmann and Wölfl thought they had shown that the radium D did not enter the organic compound, but it was concentrated in the lead: $2PbCl_2 + 4C_6H_5MgBr = (C_6H_5)_4Pb + Pb + 4MgClBr$. The author has repeated the experiments but cannot confirm these results, and can find no indication of a separation of the radium D from the lead.

Vacuum Tar.—Amé Pictet and Maurice Bouvier.—By treatment with sodium the authors have proved that vacuum tar contains alcohols, probably of the hydroaromatic series. By fractionation and removal of these alcohols by means of sodium they have obtained different fractions, two of which they have investigated. One consists of a hydrocarbon of formula $C_{10}H_{20}$, which appears to be the hexahydride of durene (1.2.4.5-tetramethylcyclohexane), while the other, of formula $C_{11}H_{22}$, has not yet been definitely identified, but may probably be the hexahydride of pentamethyl benzene.

Syntheses by Means of Organometallic Derivatives of Zinc. Preparation of α-Ketonic Acids.—E. E. Blaise.—It might be supposed that the α-ketonic ethers could be prepared by the action of the chloride of ethoxalyl on the mixed organometallic derivatives of zinc, but as a matter of fact the following reaction occurs:—

$$2C_2H_5OCOCOCl + 2RZnI = C_2H_5OCOCR_2OCOCOOC_2H_5 + 2ZnICl.$$

The indirect method of preparing the α-ketonic ethers which the author has previously described, and in which the cycloacetals are formed as intermediate products, gives good results. Thus oxyisobutyric acid is treated with ethoxalyl chloride and the raw product is heated with thionyl chloride. The condensation of the acid chloride thus obtained with a mixed organometallic derivative of zinc gives the mixed cycloacetal of the α-ketonic acid. The alcoholysis of the cycloacetal gives a mixture of oxyisobutyric ether and α-ketonic ether, which can easily be separated by fractionation.

Synthesis of Benzyl Chloride and its Homologues.—Marcel Sommelet.—When the chlorinated ether oxides $ClCH_2OCH_3$, $ClCH_2OC_2H_5$, $ClCH_2OC_3H_7$ react with benzene in presence of aluminium chloride below 0°, hydrochloric acid is evolved and the ether oxide of a benzyl alcohol is formed: $RH + ClCH_2OR' = RCH_2OR' + HCl$. At the same time some benzyl chloride is formed by the reaction $C_6H_6 + C_3H_7OCH_2Cl = C_6H_5CH_2Cl + C_3H_7OH$. It is necessary to dilute with carbon disulphide. With toluene $SnCl_4$ has to be used instead of aluminium chloride. The reaction is applicable to many benzene hydrocarbons. Toluene gives rise to the chloride of paratoluyl, and generally speaking the substitution takes place every time it is possible in the para position with reference to a side chain.

MEETINGS FOR THE WEEK.

MONDAY, 16th.—Royal Society of Arts, 8. (Cantor Lecture). "Artistic Lithography," by Joseph Pennell.

TUESDAY, 17th.—Royal Institution, 3. "Animals and Plants under Domestication," by Prof. W. Bateson, F.R.S., &c.

WEDNESDAY, 18th.—Royal Society of Arts, 8. "Preservation of Wood," by John Slater, F.R.I.B.A.

— Biochemical Society, 5.30. (In the Chemical Dept., Guy's Hospital Medical School).

THURSDAY, 19th.—Royal Institution, 3. "Hamlet in Legend and Drama," by Prof. I. Gollancz, Litt.D.

— Royal Society. "Brain of Primitive Man, with special reference to the Cranial Cast and Skull of Eoanthropus (the Piltdown Man)," by G. Elliot Smith. "Oxidases," by A. J. Ewart. "A New Malaria Parasite of Man," by J. W. W. Stephens. "Investigations dealing with the Phenomena of 'Clot' Formations—Part II., The Formation of a Gel from Cholate Solutions having many Properties analogous to those of Cell Membranes," by S. B. Schryver. "Influence of the Position of the Cut upon Regeneration in *Gunda ulvae*," by D. Jordan Lloyd.

— Chemical, 8.30. "Condensations of Cyanohydrins—Part II., The Condensation of Chloralcyanohydrin with Chloral Hydrate and with Bromal Hydrate," by H. L. Crowther, H. McCombie, and T. H. Reade. "The System Ether—Water—Potassium Iodide—Mercuric Iodide: Part II., Saturated Solutions in the Four-component System," by A. C. Dunningham. "Connection between the Dielectric Constant and the Solvent Power of a Liquid," by W. E. S. Turner and C. C. Bissett. "Viscosities of some Binary Liquid Mixtures containing Formamide," by E. W. Merry and W. E. S. Turner.

FRIDAY, 20th.—Royal Institution, 9. "Busts and Portraits of Shakespeare and of Burns—an Anthropological Study," by Prof. A. Keith, F.R.S., &c.

— Physical, 8. "Moving Coil Ballistic Galvanometer," by R. Ll. Jones. "Vibration Galvanometers of Low Effective Resistance," by A. Campbell. "Vacuum-tight Lead-seals for Sealing-in-wires in Vitreous Silica and other Glasses," by H. J. S. Sand.

SATURDAY, 21st.—Royal Institution, 3. "The Electric Emissivity of Matter," by J. A. Harker, F.R.S., &c.

THE CHEMICAL NEWS.
VOL. CIX., No. 2830.

THE PLACE OF MERCURY IN THE PERIODIC SYSTEM.

By PRAFULLA CHANDRA RÂY.

MERCURY is assigned a place in the periodic system in Group II., and regarded as a member of the magnesium-zinc family of elements. Mercuric compounds, no doubt, bear some analogy to those of magnesium, zinc, and cadmium, though by no means is it so very close. Mercury, for instance, is far less electro-positive than cadmium or zinc. Magnesium and zinc chlorides undergo hydrolysis in aqueous solution, and when evaporated to dryness give rise to basic salts with evolution of hydrochloric acid. The halides of cadmium, however, resemble the corresponding compounds of mercury as far as the non-dissociation of their aqueous solutions is concerned; moreover, cadmium, like mercury, seems to yield a lower oxide and a chloride. (Cadmous chloride and oxide have evidently been obtained in an impure condition; *vide* Morse and Jones, *Am. Chem. Journ.*, 1890, xii., 488; *cf.* Canzoneri, *Gazzetta*, 1897, [2], xxvii., 486). A zincose-zincic chloride has also recently been prepared in my laboratory by Datta and Sen (*Journ. Am. Chem. Soc.*, June, 1913, xxxv.).

As might be expected from its feeble ionisation, cadmium chloride shows many properties in common with mercuric chloride, notably its capacity to combine with ammonia and the amines, including pyridine and piperidine (Varet, *Comptes Rendus*, 1892, cxv., 464; *cf.* also Rây and Dhar, "Chlorides of the Mercurialkyl Ammonia Series, &c.," *Journ. Chem. Soc.*, 1913, ciii., 3).

While the relationship of the compounds of diad mercury with those of the zinc-cadmium family is by no means very marked, mercur*ous* compounds, on the other hand, bear the closest analogy to those of silver. As far as the halides are concerned this similarity has been noticed for a long time past. The most noticeable feature in this respect is that afforded by *mercurous nitrite*, both in its properties and in its mode of formation. As long ago as 1874, Russell noticed that when silver dissolves in nitric acid silver nitrite is formed in quantity, partly in solution in the silver nitrate liquor, partly as crystals (*Journ. Chem. Soc.*, [2], xii., 3). The stability of silver nitrite in presence of strong nitric acid is noteworthy, as ordinary nitrites are decomposed even by the weakest acids. Mercurous nitrite also is produced under similar conditions; indeed, the initial product of the action of dilute nitric acid upon mercury in the cold is the *nitrite* and not nitrate (Rây, *Zeit. Anorg. Chem.*, 1896, Bd. xii., 365; *Journ. Chem. Soc.*, 1897, 337); and the former is quite stable in presence of a concentrated solution of mercurous nitrite and nitric acid (*cf.* Rây, "Theory of Production of Mercurous Nitrite, &c.," *Journ. Chem. Soc.*, 1905, lxxxvii., 171).

Both in its chemical and physical properties, again, mercurous nitrite has been found to be the analogue of silver nitrite. So far it has been known to be the only other metallic nitrite which, with ethyl and other alkyl iodides, yields nitro-bodies of the fatty series (Rây, *Ann.*, cccxvi., 253; *Proc. Chem. Soc.*, 1899, p. 239); in fact, it can be used as an efficient substitute for silver nitrite.

The colour of compounds is often found to be a periodic function of the atomic weights of the component elements (Bayley, *Phil. Mag.*, 1882, xiii., 34). Thus silver chloride is white, while the bromide has a faint yellow tint, and the iodide is distinctly yellow. The corresponding halides of mercury also show the same relative intensity in a more pronounced manner. For example, mercurous chloride is white, the bromide yellow (mercurous bromide is often described as white, *cf.*, Strohmann, *Ber.*, 1880, xx., 2818, but its yellow colour under modified conditions has been noticed; *e.g.*, the crystalline needles are "jaunes à chaud blanchâtres à froid," Moissan, *Chim. Miner.*, T. v., 256), and the iodide intensely yellow (Rây, *Journ. Chem. Soc.*, 1897, p. 350). Silver nitrite has a pale yellow tint, but mercurous nitrite has a deep bright yellow colour. Silver and mercurous hyponitrites also show a similar gradation in the depth of colour.

In assigning the proper place to an element in the periodic system isomorphism is often an important help and guide. According to Groth the univalent metals, copper, silver, and gold, in the form of the crystallised elements, constitute an undoubtedly isomorphous group, and the first two replace each other isomorphously in a number of native silver compounds, as also in the complicated salts, the triple thiocyanates, $Cs_3SrCu_2(SCN)_7$ and $Cs_3SrAg_2(SCN)_7$, and the compounds—

$$NH_4Cl,CuCl,4(NH_4)_2S_2O_3 \text{ and } NH_4Cl,AgCl,4(NH_4)_2S_2O_3$$

("Chemical Crystallography," trans. by Marshall, p. 73). As far as one can make out, no compound of monad gold has as yet been described in which it isomorphously replaces silver or monad copper. From the close similarity of the compounds of silver to those of monad mercury as shown above, it might have been reasonably expected that they should vicariously replace each other in some cases. This expectation has also been realised. In the complex silver-mercurosomercuric oxynitrates, silver isomorphously replaces univalent mercury (Rây, *Journ. Chem. Soc.*, 1907, xci., 2033).

It will thus be noticed that while the relationship of gold with silver and mercury is at best very remote, that of monad mercury with silver is all along very close and marked. It would appear to be more rational to place monad mercury at the bottom of Group I. in the periodic system and relegate gold to its more congenial place in Group VIII. immediately after platinum. Univalent mercury should be regarded as quite a distinct metal from bivalent mercury; the former is related by ties of closest affinity to silver, while the latter can, at best, claim weak kinship with members of the second group, namely, zinc and magnesium. (It is, of course, not suggested that diad mercury should altogether be removed from its place in Group II.). In this duality of functions mercury is comparable to thallium, which, with variation in valency, affords also a remarkable instance of variation in chemical properties.

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NITROGEN AND CHLORINE IN RAIN AND SNOW.

By G. H. WIESNER.

SHUTT determined the nitrogen in the rain and snow that fell near Ottawa, Canada, during a portion of the year 1906—07. It occurred to us it might be worth while to examine the precipitations at Mount Vernon, Iowa. It is a village of 1700 inhabitants, without manufacturing industries, rather sparsely populated, so that the atmosphere is reasonably free from contamination.

The rain and snow were collected in two porcelain lined pans, each 20 inches in diameter, in an open space near the centre of the village. We tested altogether 31 samples, 22 of rain and 9 of snow.

The snowfall during this period amounted to 24 inches (two precipitations were snow and sleet), which is equivalent to 2 inches of rain. The rain during the period was 14 and eight-tenths inches, making a total of 16 and eight-tenths inches, which is above the normal precipitation for this section.

TABLE I.

Date.	Precipitation in inches.		Parts per million.				
	Snow.	Rain.	Nitrogen in nitrite.	Nitrogen in nitrate.	Chlorine.	Free ammonia.	Albuminoid ammonia.
Feb. 22	Sleet and snow	0·25	0·0035	0·15	4·8	6·00	7·00
25	3·0	—	0·002	0·13	3·2	1·28	1·92
Mar. 4	0·5	—	0·0035	0·35	4·8	7·0	8·0
5	1·0	—	0·003	0·36	7·2	5·0	5·5
7	4·0	—	0·0025	0·13	4·4	3·4	3·75
12	—	0·25	0·004	0·6	8·0	10·0	14·0
13	—	0·5	0·002	0·15	2·8	3·75	1·0
13	—	0·1	0·002	0·14	4·8	0·4	0·56
14	3·0	—	0·0015	0·11	5·2	1·0	1·0
20—21 ..	5·0	—	0·001	0·09	4·0	5·0	6·0
23	—	1·0	0·002	0·27	5·2	0·48	0·76
April 2	—	0·4	0·0015	0·24	6·0	0·68	1·12
4	1·25	—	0·002	0·25	2·0	0·96	0·96
7	Snow and rain	0·5	No trace	0·15	4·8	0·52	0·44
8	—	0·8	"	0·1	4·8	0·4	0·4
9	—	1·0	"	0·06	3·6	0·224	0·44
10	—	0·05	Not tested	0·15	4·0	0·36	0·2
May 3—4 ..	—	0·75	0·004	0·45	4·8	0·32	0·32
4—5 ..	—	1·25	0·002	0·1	4·8	0·15	0·32
5	—	1·0	No trace	0·09	4·8	0·112	0·36
8—9 ..	—	0·5	0·001	0·11	4·4	0·04	0·8
13	—	0·5	0·002	0·1	4·0	0·48	1·8
14	—	1·0	0·001	0·08	4·0	0·36	0·32
15	—	1·0	No trace	0·05	4·8	0·32	0·2
17	—	0·1	Not tested	0·07	4·0	1·0	0·36
19—20 ..	—	0·5	0·004	0·11	5·2	0·36	0·34
20	—	0·5	0·002	0·09	4·4	0·2	0·36
20—21 ..	—	0·5	0·0015	0·06	4·8	0·136	0·112
24	—	0·1	Not tested	0·1	Not tested	0·24	0·16
25—26 ..	—	2·0	0·001	0·08	4·8	0·112	0·36
June 5	—	0·75	0·001	0·2	4·0	0·36	0·75

TABLE II.

Date.	Precipitation in inches.		Pounds of nitrogen per acre.				
	Snow.	Rain.	Nitrogen in nitrite.	Nitrogen in nitrate.	Nitrogen in free ammonia.	Nitrogen in albuminoid ammonia.	Total.
Feb. 22	Snow and sleet	0·25	0·00019	0·0085	0·2802	0·32690	0·61579
25	3·0	—	0·00011	0·00687	0·05979	0·08968	0·15655
Mar. 4	0·5	—	0·00044	0·00330	0·00544	0·06622	0·07540
5	1·0	—	0·00005	0·00676	0·07785	0·08563	0·17029
7	4·0	—	0·00018	0·00983	0·21179	0·23356	0·44536
12	—	0·25	0·00022	0·03378	0·46712	0·69397	1·15509
13	—	0·5	0·00022	0·01701	0·35034	0·09342	0·46099
14	3·0	—	0·00008	0·00623	0·04671	0·04671	0·09973
20—21 ..	5·0	—	0·00009	0·00850	0·38945	0·46710	0·86504
23	—	1·0	0·00045	0·06126	0·08968	0·14574	0·29713
April 2	—	0·4	0·00013	0·02178	0·05082	0·08370	0·15643
4	1·25	—	0·00004	0·00567	0·01793	0·01793	0·04157
7	Snow and rain	0·5	No trace	0·01701	0·04735	0·02055	0·08492
8	—	0·75	"	0·01715	0·05979	0·05979	0·13673
9	—	1·0	"	0·01361	0·04185	0·08221	0·13767
10	—	0·05	Not tested	0·00170	0·00306	0·00186	0·00662
May 3—4 ..	—	0·75	0·00068	0·07582	0·04484	0·04484	0·16618
4—5 ..	—	1·25	0·00056	0·02535	0·03440	0·07474	0·13506
5	—	1·0	No trace	0·02041	0·02097	0·06726	0·10864
8—9 ..	—	0·5	0·00011	0·01257	0·00373	0·07474	0·09115
13	—	0·5	0·00022	0·01134	0·04484	0·16816	0·22456
14	—	1·0	0·00022	0·01815	0·07726	0·05979	0·15542
15	—	1·0	No trace	0·01134	0·05979	0·03737	0·10850
17	—	0·1	Not tested	0·00588	0·01868	0·00772	0·03228
19—20 ..	—	0·5	0·00045	0·01257	0·03863	0·03176	0·08341
20	—	0·5	0·00022	0·01020	0·01868	0·02863	0·05773
20—21 ..	—	0·5	0·00017	0·00680	0·01269	0·01046	0·02912
24	—	0·1	Not tested	0·00226	0·00448	0·00298	0·00972
25—26 ..	—	2·0	0·00045	0·03639	0·04385	0·15453	0·19752
June 5	—	0·75	0·00017	0·03403	0·05794	0·10510	0·18724
			0·00549	0·52412	2·70291	3·35291	6·58543

The samples were collected from February 22 to June 5, 1912. The winter months were dry up to the time the investigation was begun.

The snow of March 4 was taken from drifts on the hard crusts of the previous fall, and was not very clean. This may account for the large amount of both free and albuminoid ammonia.

The rain of March 12 was accompanied by the first thunderstorm, and the nitrogen nitrate was 0·6 part per million, the free ammonia 10 parts, and the albuminoid ammonia 14 parts. These were the highest results obtained from any sample. After this the rains were frequent until April 10. Then there was a dry period of nearly a month, and the rain of May 3 had 0·45 part of nitrogen nitrate per million. Beginning May it rained three days, and the samples were tested in three portions. The third portion had only 0·09 part of nitrogen nitrate per million, and no trace of nitrite. In general, the various substances in solution depend on the time between precipitations. The chlorine remained the same in the three precipitations, 4·8 parts per million.

In determining the nitrogen in ammonia it was computed that 1 inch of rainfall per acre weighs 226,875 pounds. Then, if the precipitation contained 0·04 part of ammonia per million, the weight expressed as millionths was multiplied by 0·04 and the product by 14/17, which gives the nitrogen in pounds per acre.

The average of the free ammonia in snow was 3·35 parts per million and in the rain 0·931 part per million.

The albuminoid ammonia in snow was 3·84 parts per million and in rain 1·13 parts per million.

The nitrogen nitrite in snow was 0·0021 part per million and in rain 0·0018 part.

In snow the average for the nitrates was 0·19 part per million and in rain 0·15 part.

The average of the chlorine in snow was 4·7 parts per million and 4·8 parts per million. The source of this is doubtless the sodium chloride from the Atlantic Ocean. As the spray is washed upon the shore it is caught by the wind and borne across the continent. Mount Vernon is about 1200 miles distant from the Atlantic Ocean.

Table I. shows the parts per million of the several constituents, and Table II. the number of pounds per acre. The total number of pounds of nitrogen per acre during the period covered by the investigations was 6·26887.

We desire to express our thanks to Dr. N. Knight for the aid he rendered in this work.

Cornell College, November 22, 1913.

THE MECHANISM OF ANODIC REACTIONS AND THE BEHAVIOUR OF IRON AND NICKEL ANODES.*

By E. P. SCHOCH,
Professor of Chemistry in the University of Texas.

(Concluded from p. 76).

In the absence of any "oxide skeleton" the layer of oxygen, on thickening, would soon allow bubbles of gas to escape—as is probably the case with platinum, iridium, &c., in which the oxide formed is within the body of the metal. But when a non conducting oxide skeleton is formed the layer of gas may accumulate to a relatively great thickness as the oxide skeleton grows, and this may prevent more or less completely the passage of any ions to the electrode. (However, such a film will still allow free electrons to pass from the electrode to the solution, which gives the pole the property of an electric *valve*). Finally, if the oxide is oxidisable to a conducting (per-)oxide, then a suitable concentration of oxygen produced by its discharge under a sufficiently great potential will produce this peroxide, and oxygen gas will then be evolved from the new surface of the peroxide. The actual existence of this latter state of affairs has been beautifully demonstrated by E. Mueller (*Zeit. Elektrochem*, xiii., 133), who showed that a copper anode in sodium hydroxide solution forms hydrated cuprous oxide as long as the current density is small enough; but with a larger current density the anodic potential becomes more noble, copper peroxide is visibly formed on the anode, and then oxygen is evolved from the surface of the latter. It appears that the "oxygen producing" discharge of ions on *peroxide* anodes is a rapid reaction, because no great hindrance is observed even with great current densities.

This beautiful demonstration by E. Mueller of the relations between active and passive copper indicates that the phenomena which characterise the attainment of passivity by some metals in certain electrolytes appears to be nothing but the regular behaviour of anodes under the existing conditions. The writer's study of the behaviour of iron and nickel anodes in various electrolytes has led him to the same conclusion with reference to the passivity of these metals. These facts will now be reviewed in the light of the general theory of anode actions outlined above.

Iron or nickel placed in solutions of their (neutral) salts will assume a definite "equilibrium" potential (*Zeit. Physik. Chem.*, lviii., 301; *Am. Chem. Journ.*, xli., 208).

When such electrodes are used as cathodes during electrolysis *alloys* of iron or nickel with hydrogen are obtained which exhibit higher (more zincic!) potentials than the equilibrium potentials of the metals.

When such electrodes are used as anodes during electrolysis, with current densities below a certain approximate limit, then only dissolution of the metal will occur, and with any one particular current density the anodic polarisation (or potential drop below the equilibrium potential) will be the same whether the particular current density is approached through a series of increasing or decreasing current densities (in the latter case even the largest current densities in the series must not have exceeded the "limit" mentioned above). In other words, current densities within this limit do not leave a "permanent" effect upon the surface of the electrode. With an electrolyte containing any one particular anion the approximate limit of these current densities which do not leave a permanent effect upon the anode is extended to greater current densities by (*a*) raising the temperature, (*b*) an increase in the concentration of the hydrogen ions or a decrease of the hydroxyl ion; (*c*) by stirring or replenishing the electrolyte on the surface of the anode. Hence the writer's experiments were made at different temperatures—most of them at 25° C., and a few at 98° C.; the concentration of the hydrogen ion was definitely known and varied from one-tenth normal acid to one-tenth normal alkali; and in all experiments the electrolyte was stirred vigorously and uniformly, and in the experiments with iron fresh electrolyte was also passed constantly through the anode chamber in order to avoid the complicating oxidation of the ferrous salt formed (*Journ. Phys. Chem.*, xiv., 739; *Am. Chem. Journ.*, xli., 235).

The particular electrolytes employed were (*a*) neutral solutions of ferrous or nickel sulphate and chloride, solutions of potassium sulphate, nitrate, perchlorate, chlorate, bromate, iodate, chromate, hydroxide, and sodium acetate; (*b*) acidified and alkaline solutions of the sulphates, nitrates, and acetates; and (*c*) mixtures of sulphate with chromate and sulphate with fluoride. Arranged in increasing order of their limits of the current densities with which the surfaces of iron or nickel anodes are not "permanently" affected, the anions present the following list:—

(*a*) Hydroxides, iodates, bromates, chlorates, chromates, with all of which only exceedingly small curren

* A Contribution to the General Discussion on "The Passivity of Metals" held before the Faraday Society, November 12, 1913.

densities do not affect the surface of the anode permanently.

(b) Nitrates.

(c) Perchlorates.

(d) Acetates.

(e) Sulphates.

(f) Halides—with the latter large current densities do not affect the surface.

With current densities beyond such limits, the action of the current produces a *permanent* effect—that is, the effect remains for a finite period of time after the current has ceased to flow, and with the same current density an iron or a nickel pole may show widely different potentials depending on its "previous history," in an uncontrollable manner. In general, it may be said that the potential of the electrode will become lower (more noble!) with the length of time that such current densities beyond the above limit continue to flow, and the potential drop will be more rapid with greater current densities than with lesser. In many cases the potential will drop almost suddenly down to the potential with which oxygen is evolved. When the surface of an electrode has been affected by electrolysis with a current density beyond the "limit," above, then an exceedingly small current density will suffice to keep its potential steady—that is, will suffice to maintain the electrode surface in the state in which it is. But when the current ceases to pass, the iron or nickel electrode immediately begins to lose its permanent effect *in all electrolytes*, and it is only a question of time until the surface is again in its original state.

These are the general facts in the behaviour of iron or nickel anodes in various electrolytes. They are readily explained by the general theory of anode action, as follows:—

With current densities below the limit mentioned, the ions are discharged upon the electrodes, where they react with velocities depending on the specific relation between each anion and each metal. When the surface of the anode is covered with discharged anions which are still in the progress of reaction, access of other anions to the surface is impeded, and the production of oxygen ions near the electrode will begin. The discharge of the latter upon the metal surface produces the permanent effect; and anything that will delay or hinder the formation of these oxygen ions will widen the limit of the current densities which do not affect the surface. An increase of temperature, as usual, will increase the velocity of reaction between the anions and the metal, and thus lessen the time during which the reacting masses cover the electrode. Stirring will help to remove the reaction-products more rapidly. An increase in the hydrogen ion concentration will lessen the tendency for the formation of oxygen ions from the other ions, so that a potential difference higher than without the acid is required to bring about the same amount of dissociation into oxygen ions. Finally, a glance at the order of the anions in the list above reveals that this also is in accord with our theoretical notions: the ions which even with small current densities permanently affect the surface are hydroxylion, iodation, bromation, chloration, chromation—the first one of which is the oxygen ion itself, and the others are just the ions which may be expected to dissociate into free oxygen ions much more readily than the others further down the list.

The loss of the "permanent" effect which iron or nickel electrodes experience in all electrolytes after the current ceases to pass is in the nature of a discharge of a short-circuited cell: the "oxygen" spots act as the positive poles, and the uncovered spots (which were previously occupied by the reacting anions) act as the negative poles.

It has thus been shown that the general facts observed in these experiments are explained satisfactorily by the theory of anode actions first outlined. In conclusion a few special remarks should be made in anticipation of possible objections raised to this theory or counter-claims made for other theories.

No special attempt was made to state in what particular form the oxygen obtained by the discharge of oxygen ions is present on the surface of iron or nickel anodes, that is, whether it is present as free oxygen or as oxide. To the writer there do not appear to be any facts which establish one view over the other (*Am. Chem. Journ.*, xli., 251). The assumption of a free oxygen film is perhaps a trifle simpler than the assumption of a formation of an oxide, but the possibility of the presence of an oxide has not been disproven even by the experiments of Mueller and Koenigsberger (*Phys. Zeit.*, vi., 847).

(NOTE.—These authors compare the reflecting power of two polished slabs of iron placed in sodium hydroxide solution. One of the slabs was "passivised" and then allowed to regain its normal state; and while it went through these changes its reflecting power was found to remain constant and the same as that of the slab which was not passivised. The fundamental error here is the assumption that the slab which was simply immersed was not acted upon; a slight electrolytic action undoubtedly took place between different spots of this slab, and the *difference* in the extent to which the slabs were affected is naturally much less conspicuous than the difference between a changed and an unchanged surface (and hence probably not observable).

Grave (*Zeit. Phys. Chem.*, lxvii., 513) has recently presented facts and arguments in support of Foerster's suggestions (*Abh. Bunsen Ges.*, No. 2) that the hydrogen in iron or nickel may be the catalyser to which they owe their activity, and hence when it is more or less completely absent these metals should be relatively inactive—passive. While it is a fact that hydrogen *alloys* with hydrogen or nickel, and that these alloys show a higher potential with higher per cents of hydrogen in them, yet these alloys really present only the same general relation which other alloys and other mixtures present. In the condensed form into which the hydrogen is probably compressed by the "surface effect" of the metal, the hydrogen itself would exhibit a potential as high or slightly higher perhaps than the alloys, and hence the potentials of the alloys thus appear to be below the potential of the "higher potential component"—a relation that is shown by all alloys. Furthermore, the activity of iron or nickel is also much greater with halide electrolytes than with others, such as sulphate electrolytes, even though hydrogen ions are equally absent in both electrolytes, and the theory of the catalytic influence of hydrogen upon these metals fails to account for this.

Possibly the best experimental evidence for a decision between this hydrogen catalysis theory and the theoretical views we have here advanced is the following.

A chromium anode that has become passive with reference to the formation of bivalent ions does not become active again to form trivalent ions, but does become active again to form chromation.

An iron anode that has been made passive with reference to the formation of bivalent ions does not become active again to form trivalent ions. However, when electrolysed in acetate or oxalate solutions the electrode becomes active again (that is, the metal dissolves again extensively) at potentials considerably below those (more noble!) at which it had ceased to be active before and at which it is usually passive in other electrolytes. The same thing is true of nickel (*Journ. Phys. Chem.*, xiv., 719; *Journ. Am. Chem. Soc.*, xxx., 1737).

In all three instances above the activity at the lower potential is due to a reaction which consumes oxygen and thus lays the metal surface bare. This is plainly the case in the formation of chromations. In the other examples the activity of the iron or nickel reappears when the potential is low enough to oxidise the acetion or oxalation, and when the oxygen is removed to oxidise these substances, then the metal surface is exposed and is subject to the attack of the anions.

THE SCIENTIFIC WEEK.

(From Our Own Paris Correspondent).

M. Edmond Perrier on Cuvier's Influence on French Science.

At the Centenary Conference of 1914 organised by the *Revue Hebdomadaire*, M. Edmond Perrier, Director of the Natural History Museum, vividly described the great physiognomy of his predecessor at the Museum. At the conclusion of his lecture, M. Perrier said:—It is difficult to exercise over science a greater influence than that of George Cuvier. It may be considered as absolute up to 1860. The whole world was moved by his tragic recital of his revolutions of the globe, and enthusiastic over his wonderful reconstruction of animal forms that to-day have completely disappeared. Naturalists admired the magnificent arrangement of his classification, and his determinations of the age of terrestrial layers opened up new roads for geologists. Since then not only the order of the superposition of these layers has been determined, but the duration of time they took to form has also been measured, and was found to be immense. Cuvier's laws of the correlation of forms have since received many a rent; the four branches have become divided; it is no longer a question of the fixity of the species. Thus the whole of Cuvier's philosophy falls through; what remains of him is the revelation of the great variety of the organisation of invertebrated animals; the resurrection of a long past of the earth; the rigorous order, the precise method introduced into all the branches of natural science; an unprecedented accumulation of new facts that might have led such a vast mind to higher conceptions if he had not voluntarily folded his wings. It is, above all, the example of a great life devoted to incessant labour for the greater value of science.

Psychology and Psychiatry.

In a lecture delivered at the College de France under the patronage of the Institute Général Psychologique, Dr. George Dumas, Professor at the Sorbonne, showed how useful the knowledge of normal psychology is to a clinician in order to make general symptomatology or special psychiatry. The lecturer then went on to study the services that psycho-analysis and laboratory psychology may render to psychiatry. While making certain critical reserves on the first of these methods and on the systematic results that a contemporary school tries to draw from them, he showed the interest that may exist for the clinician in the analytical study of a delirium, and he indicated how far experimental psychology may serve psychiatry by giving more precision and objectivity to its measures, observations, and results.

Intensity of Hertzian Waves Varies According to the Weather.

The intensity of the signals emitted by the posts of wireless telegraphy varies not only at different hours of the day, but also at different periods of the year. Extremely interesting researches on the variations of the intensity of radiotelegraphic signals have just been made by Prof. E. W. Marchand between Liverpool and Paris, and by Prof. Mossler in Germany. During a year, Prof. Mossler had measured both by day and night, by means of a detector and a galvanometer, the intensity of a current of reception in a station of wireless telegraphy situated at a distance of 425 kilometres towards the coast. He has remarked that during the day the intensity is not influenced by the height of the sun, and that this intensity remains constant for all the year, but that the characteristic maxima values are manifested during the night in autumn and in spring. In general Prof. Mossler observes that in summer one cannot reckon on a night reach of intensity much greater than of the day during the colder season. During the night very strong increases of intensity are remarked, which disappear rapidly. It would seem that they are to be attributed to the changes of ionisation of the higher atmosphere. In spite of very minute measurements no influence exercised by the brilliancy of the moon on the intensity of the signals has been observed. The observations of M. Marchand are not less curious. It is signals sent off by the Eiffel Tower at 10.45 o'clock in the morning and at 11.45 in the evening which have served him as a point of comparison. The result of these experiments shows that the maximum of variation of diurnal intensity of the signals during the same month is from 0·6 to 1·3, the average intensity being 1·1. On a fine clear night the signal has an intensity equal to 1·7 times that of the day signals. The meteorological state affects the intensity of the signals emitted and received. In Paris the rain always decreases the intensity of the reception. A wind blowing from the north-west at a speed of 6 metres per second has once lowered by one-half the normal intensity of reception. Cloudy weather is the most favourable for the transmission and reception of wireless telegraphy signals. If the sky is clear, or if there are only light clouds, the signals are weaker. The rain at the receiving station does not appear to have any great influence on the intensity of the Hertzian waves. A curious fact observed by M. Marchand and by the officers of the military wireless telegraphy is the strengthening of the intensity of the signals immediately after sunset, which increase has sometimes amounted to 70 per cent. The intensity of the signals remained constant after the sudden strengthening. The explanation of these diverse phenomena still remains mysterious.

Invasion of Oysters from Portugal.

Portuguese oysters, which according to the opinion of zoologists do not even belong to the properly called species of oysters but to the gryphæa species, are threatening to invade the French oyster beds. M. Edmond Perrier, Director of the Natural History Museum, recalls to mind that the more robust Portuguese oysters have, in the region of Arcachon, supplanted the native oysters, which have a much finer taste. The Portuguese oysters are likewise attacking the Marennes oysters that are so highly appreciated. But it was thought that the danger was limited. It was not thought that the Southern gryphæa could become acclimatised on the Brittany coasts. Now such is not the case. The Portuguese oysters can very well live on the Brittany coasts, and they are threatening to gradually take the place of the oysters of Cancale that have a much better taste and are more appreciated. M. Dantan, who has made numerous studies on these molluscs, indicates, however, a means which will enable oyster cultivators to guard against the danger. This means is founded on the notable difference between the embryo of the ordinary oyster and of the Portuguese oyster. The embryo of the ordinary oyster develops inside the shell, whereas the embryo of the Portuguese, more undisciplined, comes out of the shell and goes and fixes itself on the collectors; that is to say, on the posts, fascines, tiles that are employed to collect the "naissin" or spawn. Indeed, the larva only develops on the surface. If, then, the collectors are driven down deeper, the embryos of the Portuguese oysters will no longer be able to live. The peril will thus be averted.

Mountain Sickness.

Some curious experiments on mountain sickness have been made by Dr. Guillemard, by the help of rabbits transported during the compaigns from the plain to the top of Mont Blanc, at an altitude of 4800 metres, and to the Marguerite hut, situated at the top of Mont Rose, at an altitude of 4560 metres. M. Armand Gautier remarks in the communication that he presents before the Academy, in the name of M. Guillemard, that the ureic nitrogen increases notably in the blood from the third day. The non-ureic nitrogen and the total nitrogen likewise increase. These phenomena seem to indicate that mountain sickness

is the result of a nitrogen intoxication. The urea, a toxic substance that should be eliminated by the kidneys, is retained by the organism. It is thus a veritable poisoning that occasions mountain sickness.

Transparency of Leaves to Ultra-violet Rays.

M. Dangeard has studied the transparency of leaves *vis à vis* to ultra-violet rays supplied by a mercury vapour lamp. He has observed, according to Prof. Mangin, that in a certain number of plants, particularly ferns, the leaves are much more transparent than glass for these rays. This is a somewhat remarkable result, if we consider that leaves have a complex structure. Begonia leaves and those of the China primrose have, on the contrary, the same transparency as glass for the ultra-violet radiations; moreover, there are other leaves that hardly let anything more pass than the extreme radiation of the visible spectrum more or less attenuated.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, February 5th, 1914.

Sir William Crookes, O.M., President, in the Chair.

Papers were read as follows:—

"*Conduction of the Pulse Wave and the Measurement of Arterial Pressure.*" By Prof. L. Hill, F.R.S., J. McQueen, and M. Flack.

"*Report of the Monte Rosa Expedition of 1911.*" By J. Barcroft, F.R.S., M. Camis, C. G. Mathison, F. Roberts, and J. H. Ryffel.

I. Curves representing the equilibrium between oxygen and hæmoglobin were determined for *resting* individuals at Col d'Olen and the Capanna Margherita.

These and all others were capable of representation by the equation—

$$y/100 = \frac{Kx^n}{1 \times Kx^n}.$$

y = percentage saturation of hæmoglobin with oxygen.
x = oxygen pressure.
K = equilibrium constant of reaction.
n = average number of molecules of Hb assumed to be in an aggregate.

Notwithstanding a fall in the CO_2 pressure of the blood, no change in K could be detected, except as the mean of a large number of observations, when a slight fall in K, indicating decreased alkalinity of the blood, was apparent. The curves were determined in the presence of the existing alveolar CO_2 pressure.

II. The blood was investigated similarly after *exercise*, which usually consisted in climbing 1000 feet.

Climbs were made by the same individuals at—

1. Carlingford, co. Louth, from sea-level.
2. Col d'Olen, from 9000 feet.

A diminution in K invariably occurred. Climbing at a given rate the reduction in K was much greater at high altitudes. A given reduction in K involved much more rapid climbing at low altitudes. The change in K caused by *exercise*, whether at high or low altitudes, was entirely accounted for by the production of lactic acid.

Determinations of the hydrogen ion concentration in the blood of one have been made. These show a defined relation between C_H and K, so that the one may be calculated from the other.

"*Some Notes on Soil Protozoa.*" (Part I.). By C. H. Martin and K. Lewin.

It seems generally agreed that further examination of the Amœbæ will necessitate splitting up the genus *Amœba*. The first and much needed step in this reform has already been taken by Chatton by the formation of the genus *Vahlkampfia* for the group of Limax Amœbæ. Whether it would not be better to put this genus, and all other Amœbæ which show a flagellate stage in their life-cycle apart from the gamete stage, into the group Proteomyxa seems to us an open question.

There can be no doubt that in this genus *Vahlkampfia* a number of quite definite species are included which can probably be best separated by minute differences in the behaviour of the nucleus during division. It will probably be found necessary in the same way to form another genus for the Lamellipodia group, which would again have to be broken up into a number of species in a similar manner.

The main purpose of this introductory paper is not the study of these Amœbæ from a specific point of view, so much as the proof which we hope to have brought of the existence of a relatively frequent trophic Protozoan fauna in certain soils, and the rough indication of possible methods of dealing with this fauna. How far this fauna, under certain conditions, exercises a deleterious influence on plant growth is a question for the agriculturist rather than the zoologist.

The startling success in the Lee Valley of the treatment of sick soils by partial sterilisation, introduced by Russell, would seem to present a very strong argument in favour of the view that these Protozoa do exercise an important influence on plant growth in these soils. We have been able to establish the occurrence of a trophic Protozoan fauna in certain field soils that we have examined, and to this question we hope to return in a future paper.

"*Development of the Starfish*, Asterias rubens, L." By J. F. Gemmill.

"*Floral Mechanism of* Welwitschia mirabilis (*Hook*)." By A. H. Church, D.Sc.

CHEMICAL SOCIETY.

Ordinary Meeting, January 22, 1914.

Prof. W. H. Perkin, LL.D., F.R.S., President, in the Chair.

(Concluded from p. 81).

15. "*The Volatile Oil of* Cymbopogon coloratus *from Fiji.*" By Ernest Goulding and John Campbell Earl.

The essential oils derived from certain species of Cymbopogon are well known in commerce as "lemon-grass" and "citronella" oils. The former are derived mainly from *Cymbopogon flexuosus*, Stapf, and *C. citratus*, Stapf, and the latter from *C. nardus*, Rendle. The chief constituent of the lemon-grass oils is citral, the proportion of which is commonly between 70 and 80 per cent. The citronella oils, on the other hand, are characterised by the presence of considerable quantities of citronellaldehyde and geraniol, but contain very little or no citral.

In the course of a study of the various grass oils at the Imperial Institute, three oils have been encountered which have not hitherto been described, and exhibit characters very different from those of either the lemon-grass or citronella oils. One of these is furnished by the leaves of *Cymbopogon coloratus*, Stapf, and contains considerable quantities of citral and geraniol, but no citronellaldehyde.

In 1907, seeds of a lemon-grass were forwarded to Fiji from India, and the plant, since identified as *Cymbopogon coloratus*, Stapf, has been grown at Nasinu Experiment Station. It has been found by Knowles (*Bull.* No. 6, Dept. Agric., Fiji) that the fresh leaves of this grass, when distilled with steam, yield about 0·35 per cent. of oil. Samples of oil distilled in Fiji were forwarded to the Imperial Institute in 1908 and 1909, and were subjected to a preliminary investigation (*Bull. Imp. Inst.*, 1912, x., 27),

subsequently the oil was examined by Umney (*Perfumery and Essential Oil Record*, Dec., 1912, p. 317), who found it to contain 35 per cent of citral and 30 per cent of geraniol. A further sample of the oil has been received recently from Fiji, and has been submitted to examination, with the following results:—

The oil had $D^{15}/_{15}$ 0·912 and $[\alpha]_D$ at 24°, −10·31°, and contained 23 per cent of geraniol (estimated by the phthalic anhydride method). It was shaken successively with sodium carbonate, sodium hydrogen sulphite, and sodium hydroxide, and the residual oil was afterwards submitted to fractional distillation. The sodium carbonate solution extracted 0·75 per cent of the oil, consisting chiefly of acetic acid. The sodium hydrogen sulphite removed 34 per cent of aldehydes, but some of the aldehyde remained in the residual oil (see below). The aldehydic constituents had a pleasant lemon-like odour, and consisted almost entirely of citral. The treatment with sodium hydroxide extracted 0·75 per cent of phenolic substances, from which a small quantity of a white tasteless and odourless solid (m. p. 142°, decomp.) was isolated; the remainder consisted of a dark brown liquid with an odour recalling that of cloves, but the quantity was too small to admit of identification.

The residual oil still possessed a lemon-like odour, and an aldehyde estimation made by the sulphite method showed an absorption of 11 per cent. It furnished the following constants:—$D^{15}/_{15}$ 0·915; α_D 22 −12° 29′ (in 1-dcm. tube); ester value 42 (corresponding with 14·7 per cent of geranyl acetate and equivalent to 9·5 per cent in the original oil); saponification value after acetylation, 183 (corresponding with 43·4 per cent of alcohols, calculated as $C_{10}H_{18}O$). On distillation under 10—12 mm. pressure, the following fractions were obtained:—

Fraction.	Temperature.	Quantity, per cent.	$D^{15}/_{15}$.	Optical rotation, in 1 dcm. tube.
A	Up to 80°	8·3	0·858	−52° 22′
B	80—105°	2·7	0·868	38° 35′
C	105—120°	27·1	0·902	12° 55′
D	120—130°	25·5	0·912	6° 4′
E	130—150°	13·7	0·937	4° 32′
F	Residue and loss	22·7	—	—

Fraction A consisted largely of terpenes. A further quantity of terpenes was obtained by distilling some of the original oil on the water-bath under 15—20 mm. pressure. By this means a fraction amounting to 7·4 per cent of the original oil was obtained, which after repeated treatment with sodium and re-distillation had $D^{15}/_{15}$ 0·854, α_D 20 −62° 39′ (in 1-dcm. tube), and b. p. 168—173°/760 mm. The terpenes absorbed bromine to an extent corresponding with about 3 atoms per mol. $C_{10}H_{16}$, but the product could not be obtained in a crystalline state. It is probable that the terpenes were a mixture of *l*-limonene with one or more other terpenes, but the quantity of oil available was not sufficient to enable them to be identified.

Fraction B appeared to contain the constituents of A and C, and was not examined in detail.

Fraction C consisted chiefly of geraniol.

Fraction D contained more than 20 per cent of esters. After hydrolysis, it yielded a homogeneous crystalline diphenylurethane of geraniol (m. p. 82°). The readiness with which this derivative crystallised indicated the absence of citronelloldiphenylurethane.

Fraction E was readily soluble in less than three volumes of 70 per cent alcohol (indicating the absence of sesquiterpenes), and furnished geranioldiphenylurethane (m. p. 82°).

The residue F was dark brown and viscous. When submitted to distillation in steam, about one-fourth of it distilled over; the remainder probably consisted of resinous non-volatile polymerisation products formed during the distillation and fractionation of the oil.

The results of this investigation indicate that the oil of *Cymbopogon coloratus* has the following approximate composition:—

	Per cent.
Terpenes	7·5
Aldehydes, chiefly or entirely citral	40
Geraniol	23
Esters, chiefly geranyl acetate	10
Acetic acid	0·75
Phenols	0·75
Substances not identified	18

16. "*The Hydrolysis of Mixed Secondary Amides by Alkalis.*" By Arthur Walsh Titherley and Leonard Stubbs.

A mixed secondary amide, R·CO·NH·CO·R′, under the influence of alkali, may conceivably suffer hydrolysis in two possible ways:—(1) Giving $R\cdot CO_2H$ and $R'\cdot CO\cdot NH_2$, or (2) giving $R\cdot CO\cdot NH_2$ and $R'\cdot CO_2H$. Direction (1) is followed exclusively when R′ is an aromatic radicle and R is methyl, and this is attributed by the authors to stearic influence. The mechanism of hydrolysis is probably one in which water-addition first takes place at the double link (C:N) of the tautomeric form of the secondary amide, yielding $R\cdot C(OH)_2\cdot NH\cdot CO\cdot R'$, which then decomposes into the acid $R\cdot CO_2H$ and amide $R'\cdot CO\cdot NH_2$. Accordingly, in the equilibrium—

$$\underset{\text{I.}}{R\cdot C(ONa){:}N\cdot CO\cdot R'} \rightleftharpoons \underset{\text{II.}}{R\cdot CO\cdot N{:}C(ONa)\cdot R'}$$

the rate of hydrolysis of I. is very much greater than that of II., and owing to continual disturbance of the equilibrium it is the only form the hydrolysis of which can be detected. Whilst the hydrolysis of diacetamide, acetylcarbamide, and acetobenzamide in the cold is complete within forty minutes, that of purely aromatic secondary amides under the same conditions requires about fifteen hours. The influence of spacial protection on the course of the hydrolysis is illustrated by the fact that benzo-*o*-toluamide, $Bz\cdot NH\cdot CO\cdot C_6H_4\cdot CH_3$, yields benzoic acid and *o*-toluamide exclusively, whilst benzo-*p*-toluamide decomposes in both possible ways, yielding a mixture of benzoic and *p*-toluic acids, together with benzamide and *p*-toluamide. Although steric influence is potent in directing the course of hydrolysis of a mixed secondary amide, evidence is available that the affinity for water of the double link (C:N) is also a factor. In the hydrolysis of acetylcarbamide, which yields acetic acid and carbamide almost quantitatively, it is probable that the form $CH_3\cdot C(ONa){:}N\cdot CO\cdot NH_2$ only is involved. The two benzotoluamides above were obtained best by the condensation of the corresponding phenyl toluates and benzamidine, and subsequent hydrolysis of the resulting toluoylbenzamidines, $NH{:}CPh\cdot NH\cdot CO\cdot C_6H_4Me$.

17. "*The Miscibility of Azobenzene and Azoxybenzene in the Solid State and the supposed Existence of a Stereoisomeride of Azobenzene.*" By Harold Hartley and John McArthur Stuart.

An examination of the freezing-point and melting-point curves of mixtures of azobenzene and azoxybenzene has shown that these substances form two series of mixed crystals with an eutectic temperature of 24·5°. The two mixed crystals deposited at this temperature contain respectively 45 per cent and 90 per cent of azoxybenzene molecules. The latter crystals are probably identical with the substance obtained by C. V. and R. A. Gortner (*Journ. Am. Chem. Soc.*, 1910, xxii., 1294) as a by-product in the preparation of azobenzene by the distillation of azoxybenzene with iron filings, and thought by them to be a stereoisomeride of azobenzene.

18. "*The Influence of Colloids and Fine Suspensions on the Solubility of Gases in Water. Part IV. Solubility of Nitrous Oxide at Pressures Lower than Atmospheric.*" By Alexander Findlay and Owen Rhys Howell.

In continuance of previous work (*Trans.*, 1910, xcvii., 536), the solubility of nitrous oxide in water in the presence of ferric hydroxide, dextrin, starch, gelatin, egg-albumin, silicic acid, finely-divided silica, and finely-divided charcoal, has been determined at pressures lower

than atmospheric. The values obtained fit in well with those previously obtained at higher pressures, and the general type of solubility curve obtained is similar to that found in the case of carbon dioxide (*Trans.*, 1910, xcvii., 536; 1913, ciii., 636); that is to say, the solubility curves show a more or less pronounced minimum.

19. "*The Action of Aldehydes on the Grignard Reagent.*" By JOSEPH MARSHALL.

It has been found that the addition of two molecular proportions of benzaldehyde to one molecular proportion of magnesium methyl iodide results in the formation of a-methyldeoxybenzoin, $C_6H_5{\cdot}CH(CH_3){\cdot}CO{\cdot}C_6H_5$.

The course of this reaction is indicated by the equations—

$$C_6H_5{\cdot}CH(CH_3){\cdot}OMgI + C_6H_5{\cdot}CHO = \\ = C_6H_5{\cdot}CH(CH_3){\cdot}C(C_6H_5)(OH){\cdot}OMgI,$$

$$C_6H_5{\cdot}CH(CH_3){\cdot}C(C_6H_5)(OH){\cdot}OMgI + H_2O = \\ = C_6H_5{\cdot}CH(CH_3){\cdot}CO{\cdot}C_6H_5 + H_2O + Mg(OH)I.$$

A similar result was obtained when benzaldehyde was allowed to react with magnesium dimethylcarbinyl iodide, in which case phenyl *iso*propyl ketone was isolated. When, however, two molecules of benzaldehyde were caused to react with one molecule of magnesium phenyl bromide, the products of the reaction were benzyl alcohol and benzophenone, instead of phenyldeoxybenzoin (triphenylvinyl alcohol), as was expected. This result may be explained by assuming that the triphenylvinyl alcohol is hydrolysed under the conditions of the experiment as follows:—

$$(C_6H_5)_2C{:}C(OH){\cdot}C_6H_5 + H_2O = \\ = (C_6H_5)_2CO + C_6H_5{\cdot}CH_2{\cdot}OH.$$

An analogous equation would explain the production of acetophenone when acetaldehyde is allowed to react with magnesium phenylmethylcarbinyl bromide.

An attempt was made to obtain phenylmethylacetaldehyde by allowing trioxymethylene to react with magnesium phenylmethylcarbinyl iodide, but the product of this reaction was phenylethyl iodide. Similar products were obtained when ethyl formate reacted with Grignard reagents, instead of the substituted acetic esters which were expected in these reactions.

20. "*The Use of Sulphuryl Chloride in the Alkylation of Phenols.*" By WILHELMINA REBECCA SMYTH.

In view of the poisonous character of methyl sulphate, experiments have been carried out to ascertain whether it would be possible to use methyl alcohol and sulphuryl chloride in place of methyl sulphate as a methylating agent, and also whether other alcohols than methyl alcohol would react with phenols in the presence of sulphuryl chloride. The sulphuryl chloride was added to a slight excess of the alcohol, and when action was at an end the phenol was introduced. The mixture was allowed to remain for some time, and then treated gradually with a slight excess of alkali hydroxide. The ether formed was either extracted from the alkaline solution or removed by distillation in steam. In some cases before introducing the sulphuryl chloride the alcohol was treated with the calculated amount of metallic sodium, but this addition was not found to have any appreciable influence on the result. In other cases the sulphuryl chloride was cooled in a freezing mixture, and the alcohol slowly added, but here also the yields were not affected to any great extent.

The phenols treated in this way were phenol, catechol, carvacrol, and β-naphthol, the alcohols used being methyl and ethyl alcohol, and, in the case of the two last compounds, propyl alcohol. In all these cases alkylation occurs under the conditions just described, but, except in the case of β-naphthol, the ethers are only formed in small amounts. β-Naphthol yields about half the calculated amounts of the methyl, ethyl, and propyl ethers. Phenol gave from 15 to 25 per cent of anisole and phenetole, and catechol about 20 per cent of guaiacol, but no veratrole. Carvacrol gave only traces of the methyl, ethyl, and propyl ethers. In most cases practically the whole of the unchanged phenol could be recovered from the alkaline solution.

Attempts to alkylate amino-compounds in a similar manner were not successful.

21. "*The Colours produced on Mixing the Alkyl Nitrites with Substances containing Centres of Residual Affinity.*" By ERNEST MAGOWAN HARPER and ALEXANDER KILLIN MACBETH.

In view of the fact that many colour reactions have recently been obtained with the organic nitro-compounds, it appeared of interest to the authors to examine the alkyl nitrites. It was shown that these give colours with amino-compounds, ethylenic hydrocarbons, and substances containing bivalent sulphur. These colours are similar to those obtained with tetranitromethane when treated with the same substances. It is thought probable that the colour is due to an intermediate additive compound, the true final additive compound being colourless. Parallel to this is the Vorländer hypothesis, which deals with such cases to account for the two products when an acid reacts with an αβ-unsaturated ketone.

The final additive products of the nitrites and the primary, secondary, and tertiary amines have been isolated by Rây and Datta, Rây and Rakshit, and by Neogi, and the preparation of the corresponding compounds in case of the bivalent sulphur substances is being undertaken by the authors.

22. "*The Progressive Bromination of Toluene.*" By JULIUS BEREND COHEN and PAVITRA KUMAR DUTT.

Cohen and Dakin (*Trans.*, 1901, lxxix., 1111) studied the progressive chlorination of toluene through successive stages from the hydrocarbon to the tetrachloro-derivatives. The results described by A. K. Miller (*Trans.*, 1892, lxi., 1023) on the bromination of *o*- and *p*-bromotoluene present certain differences in the quantity and character of the products when compared with those obtained by chlorination of the corresponding chlorotoluenes. The authors have therefore submitted the subject to a careful investigation, in which they have determined the character of all the bromine derivatives obtained by brominating the hydrocarbon and its mono- and di-bromo-derivatives.

The results of chlorination and bromination are given side by side in the following table for comparison, the principal product being placed first in each case, those occurring in smaller quantity standing next in order, whilst a trace is indicated by brackets.

Substance taken.	Bromination products.	Chlorination products.
Toluene.	Ortho, para, (meta).	Ortho, para.
	Monohalogen Compounds.	
Ortho	2 : 5, 2 : 4	2 : 4, 2 : 3, 2 : 6, (2 : 5)
Meta	2 : 5, 3 : 4, (3 : 5)	2 : 5, 3 : 4
Para	2 : 4, 3 : 4	2 : 4, 3 : 4
	Dihalogen Compounds.	
2 : 3	2 : 3 : 6, 2 : 3 : 5	2 : 3 : 4
2 : 4	2 : 4 : 5, (2 : 4 : 6)	2 : 4 : 5, 2 : 3 : 4, (2 : 4 : 6)
2 : 5	2 : 4 : 5, (2 : 3 : 6)	2 : 3 : 6, 2 : 4 : 5
2 : 6	2 : 3 : 6	2 : 3 : 6
3 : 4	2 : 4 : 5, (3 : 4 : 5)	2 : 4 : 5
3 : 5	2 : 3 : 5	2 : 3 : 5

Attention was directed to the difference in orienting effect produced by chlorination and bromination of the ortho-halogen derivatives, which is most marked in the case of the *o*-bromotoluene and in that of the 2 : 3- and 2 : 5-dihalogen derivatives.

23. "*The Absorption Spectra of some Mercury Compounds.*" By CECIL REGINALD CRYMBLE.

It has been shown that groups attached to the mercury atom increase its absorptive power in the following order:—CN, Cl, $C_2H_3O_2$, $C_3H_5O_2$, Hg, Br, NO_2, I, and that the absorption of the molecule depends on an interaction between the mercury atom and the attached groups.

Entrance of the mercury atom into complex haloid salts is accompanied by an increase in absorptive power. It is possible to determine the nature of the complex formed, and to follow its progressive dissociation on dilution. The complex $MHgX_3$ is formed quantitatively at decimolecular concentrations in alcohol. There is no spectroscopic evidence of the formation of any higher complex, such as M_2HgX_4, in either alcohol or water.

The change in the properties of the mercury atom on passing from the dihaloid salt to the dialkyl compound has been compared with the corresponding change in the absorption spectra of these compounds.

24. "*A New Phosphoric Ester obtained by the Aid of Yeast-juice.*" (Preliminary Note). By ARTHUR HARDEN and ROBERT ROBISON.

In the preparation of hexosediphosphoric acid from lævulose and disodium hydrogen phosphate a second phosphoric acid derivative is also obtained. This is found in the filtrate after the separation of the diphosphate by treatment with lead acetate, and is precipitated on the addition of a solution of basic lead acetate. A portion of the new compound is also precipitated along with the lead hexosediphosphate, from which it can be separated by decomposing the salt with hydrogen sulphide, reprecipitating with lead acetate, and repeating these operations several times.

By decomposing the basic lead salt with hydrogen sulphide an aqueous solution of the acid itself may be prepared. It gives Seliwanoff's reaction, reduces Fehling's solution, and yields an osazone. It is strongly dextrorotatory, the specific rotation being very much higher than that of hexosediphosphoric acid. When the solution is boiled phosphoric acid is liberated, and the rotatory power falls, whilst the reducing power is slightly increased.

The barium salt was obtained by neutralising the solution of the acid with baryta, filtering, and adding an equal volume of alcohol, whereupon the salt was precipitated as a white amorphous solid. It is readily soluble in both hot and cold water, differing in this respect markedly from barium hexosediphosphate. Various methods of purification have been employed, but the salt has not yet been obtained entirely free from nitrogenous impurities. The results of analyses, however, approximate fairly closely to those required for the barium salt of a hexosemonophosphoric acid, $C_6H_{11}O_5{\cdot}PO_3Ba$.

A similar compound is also obtained when dextrose is substituted for lævulose, but it has not yet been ascertained whether these two compounds are or are not identical. The investigation is being continued, and the relations of this substance to hexosediphosphoric acid and to the process of alcoholic fermentation are being studied.

SOCIETY OF CHEMICAL INDUSTRY.
(LONDON SECTION).

Ordinary Meeting, February 2, 1914.

Prof. W. R. E. HODGKINSON in the Chair.

THE following papers were read and discussed:—

"*Estimation of Zinc in Coinage Bronze by Volatilisation.*" By T. K. ROSE, A.R.S.M., D.Sc., Chemist and Assayer of the Mint.

This old process, discontinued about 1870, has recently been revived. It consists in heating 1 grm. of the alloy for two hours in a reducing atmosphere, at a temperature of 1375°, and weighing the residue. This sample is placed in a carbon crucible with a closely fitting lid, and 8 to 16 of these are embedded in charcoal in a graphite pot and heated in an injector furnace. Coinage bronze consists of copper 95, tin 4, zinc 1, and the loss of weight under the conditions used amounts to 1·2 or 1·3 per cent, about 0·03 per cent of zinc being retained in a residual metal. Proof assays consisting of portions of a trial plate of known composition are included in each charge. The corrected results differ from each other by from 0 to 0·1 per cent, the average difference being about 0·02 or 0·03 per cent.

A few determinations of zinc in alloys containing various amounts of zinc up to 90 per cent have also been made, and found to agree with results obtained by the gravimetric and volumetric methods. As the amount of zinc is increased from 1 to 90 per cent the loss of copper rises from 0·2 to 0·4 per cent.

Sources of error are the presence of cadmium, oxygen, &c., which are reckoned as zinc, and occasionally black scales, probably sulphide of copper, adhering to the residue. Such assay pieces are rejected. Other errors are eliminated by the use of proofs. The advantage of the method is the saving of time, which is considerable, the personal time of the assayer being occupied for only three to five minutes for each determination.

"*Nickel Tannates.*" By PURAN SINGH.

The author finds that by precipitating a solution of nickel hydroxide in ammonia salts with tannic acid solution, the nickel being in excess, a greenish white precipitate slowly changing into deep brown is produced. When dry this is blackish brown. This salt contains about 28 per cent of NiO, and may be $Ni_3(C_{14}H_7O_9)_2$. When the nickel hydroxide solution is added to a tannic acid solution, the latter being in excess, an almost white salt, which slowly acquires a greenish yellow tinge, is precipitated. This contains not more than about 10 per cent of NiO, and would appear to be the normal salt, $(C_{14}H_8O_9)Ni$.

The author states that though it has not been possible to obtain absolutely pure salts, it can be safely said upon the results obtained that only two theoretical salts have been proved.

"*Oxygen and Metallic Antimony in Crude Antimony.*" By W. R. SCHOELLER, Ph.D.

Crude antimony, containing antimony 73·56 per cent and sulphur 22·45 per cent, was fused in a current of hydrogen sulphide; water was given off which was collected and weighed. 3·18 per cent of oxygen was thus found, and the crude after fusion assayed antimony 71·13 per cent, sulphur 27·56 per cent. Boiling tartaric acid solution dissolved four-fifths of the antimony combined to oxygen, which proved to be present as antimonious oxide. On repeatedly extracting the crude with hot strong hydrochloric acid, a residue assaying 97·17 per cent of antimony was obtained. The amount of metal present, as calculated from the results of the analysis, was 2·54 per cent.

The presence of antimonious oxide in crude antimony is due to absorption of oxygen by the molten sulphide, while the simultaneous presence of metallic antimony makes it more than probable that, contrary to the accepted view, antimonious oxide reacts upon the sulphide with formation of metal and sulphur dioxide, though the reaction takes place only to a limited extent.

SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

Annual General Meeting, February 4, 1914.

THE following were elected the Officers and Council for the ensuing year:—

President—A. Chaston Chapman.

Past-Presidents—Leonard Archbutt, Edward J. Bevan, Bernard Dyer, Thomas Fairley, Otto Hehner, R. R. Tatlock, E. W. Voelcker, J. Augustus Voelcker.

Vice-Presidents—George Embrey, J. T. Hewitt, H. Droop Richmond.

Hon. Treasurer—Edward Hinks.

Hon. Secretaries—P. A. Ellis Richards, Rudolf Lessing.

Other Members of Council—E. M. Chaplin, J. H. Coste, G. H. Gemmell, Charles A. Keane, G. D. Lander, Thomas Macara, L. Myddelton Nash, Cecil Revis, Harry

Silvester, Arnold R. Tankard, Thomas Tickle, John White.

Ordinary Meeting, February 4, 1914.

Mr. CHASTON CHAPMAN, President, in the Chair.

Messrs. Alan Milsom Bailey, Arthur Leslie Barton, Thomas Sidney Haines, and Arthur George Abraham Miller were elected members of the Society.

Certificates were read for the first time in favour of Messrs. Robert Bickerstaffe, Chilterns, Wooburn Green, Bucks; Thomas Henry Byrom, 58, Hornsey Rise, Crouch End, London, N.; Sydney George Clifford, 3, Norman Villas, East Dulwich, S.E.; Donald Richard Frazer, Zeitzer Strasse 9, IV., Leipzig, Germany; and John McLaren, 7, Fauconberg Road, Chiswick, London, W.

Certificates were read for the second time in favour of Messrs. Rowland Holliday Ellis and Armand de Waele.

The following paper was read:—

"*Iodometry of Arsenic, Copper, and Iron.*" By G. D. LANDER and J. J. GEAKE.

Cupric and ferric salts do not liberate iodine from potassium iodide in the presence of Rochelle salt and sodium bicarbonate. The quick volumetric process of Avery and Beans for arsenic copper mixtures is based on this fact. The authors have extended this method in the cases of copper and iron. Cuprous salts are oxidised by iodine in the presence of tartrate and bicarbonate, but in the case of ferrous salts this reversed action is incomplete.

NOTICES OF BOOKS.

Introduction to Modern Inorganic Chemistry. By J. W. MELLOR, D.Sc. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1914.

THIS book is an introduction to the author's earlier work on inorganic chemistry, than which no better text book of its scope exists. The special aim of developing in the student a thoroughly scientific attitude of mind should be admirably fulfilled, and the use of the book should certainly inculcate habits of careful reflection and accurate deduction. Every device by which vivid impressions can be made upon the young student's mind is employed; such as variations of type, short sections dealing with one or two important points only, excellent diagrammatic illustrations, and the historical development of the subject is closely followed. Important discoveries and generalisations are usually associated with the name of some great chemist or physicist, and apposite quotations from classical scientific literature are frequently given. At the end of each chapter sets of questions are given; many of these are taken, in some cases with slight modifications, from public examination papers.

The Chemistry of Cattle Feeding and Dairying. By J. ALAN MURRAY, B.Sc. (Edin.). London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1914.

IN order to be able to use this book profitably the agricultural student should possess a sound knowledge of the rudiments of inorganic and organic chemistry, and should also be well grounded in the elements of mathematics. Given these qualifications he will be able to get a thoroughly scientific view of the problems of cattle feeding from the book. Much stress is laid upon quantitative work, and all practical advice as to feeding for milk production, fattening, &c., is based upon reliable statistics and calculations. The methods of graphic solution of problems connected with the compounding of foods are novel and interesting, and the chapter on the valuation of feeding stuffs and the table giving their average composition with the cost per food unit will be very useful to the farmer.

Elements of Water Bacteriology. By SAMUEL CATE PRESCOTT and CHARLES EDWARD AMORY WINSLOW. Third Edition. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1913.

THIS book is intended for the use of students who, having some knowledge of general bacteriology, are ready for more advanced work in special branches. It is avowedly devoted chiefly to the consideration of American methods of investigation and interpretation, which however do not differ widely from those employed in England. The subject is treated in considerable detail, and an exceptionally complete bibliography is provided. A good deal of fresh matter will be found in the third edition, and a new chapter has been added dealing with the application of bacteriology to the sanitary study of shellfish, based largely upon the recent Report of the Committee of the Laboratory Section of the American Public Health Association.

The Analysis of Black Powder and Dynamite. By WALTER O. SNELLING and C. G. STORM. Washington: Government Printing Office. 1913.

THIS bulletin gives an outline of the methods of analysis employed in the laboratory of the Bureau of Mines in the examination of certain classes of explosives, *e.g.*, ordinary dynamite, ammonia, gelatin, low-freezing and granular dynamites, and common grades of black gunpowder and black blasting powder. It will be a valuable guide for all who are interested in the analysis of explosives and their use in mining work, more especially as the details of the methods actually employed in the laboratories of explosives factories are often treated as trade secrets, while the descriptions of processes to be found in text-books are frequently insufficiently full.

The Prevention of Waste of Oil and Gas from Flowing Wells in California. By RALPH ARNOLD and V. R. GARFIAS. Washington: Government Printing Office. 1913.

IT is well known that the "coming in" of wells producing large quantities of oil and gas by natural flow is usually accompanied by great waste, and the Bureau of Mines has been conducting a series of investigations which aim at minimising these losses and also at preventing damage to productive oil and gas strata by the percolation of artesian waters into them. These investigations and their results are shortly discussed in this technical paper, both preventive and remedial measures being described. Special attention is paid to the methods of J. A. Pollard, which have been very successfully employed in the Buena Vista Hills.

Heavy Oil as Fuel for Internal Combustion Engines. By IRVING C. ALLEN. Washington: Government Printing Office. 1913.

THIS bulletin describes the results of the examination of the question of the practicability of more effectively burning the heavy asphaltum oils of the Pacific and Gulf Coasts of the United States. Although the results must be regarded as somewhat tentatively put forward, since the heavy oil engine has not yet by any means attained it fullest development, it has been definitely proved that petroleums containing up to 20 per cent of asphaltum can be used for running the engines. The bulletin contains specifications of the fuels and lubricants which may be used for internal combustion engines of the heavy oil type, and epitomises the advantages of such engines over steam and explosion engines for marine purposes.

Brief Biography and Popular Account of the Unparalleled Discoveries of T. J. J. See, A.M., Lt.M., Sc.M. (Missou); A.M., Ph.D. (Berol). By W. L. WEBB. Lynn, Mass.: Thos. P. Nichols and Son. 1913.

PROF. SEE, who has done some remarkable work the value of which has been fully recognised on all sides, has found in Mr. W. L. Webb an enthusiastic biographer, who

expresses himself occasionally in somewhat extravagant language. The incidents of Prof. See's early life and of his academical career are reproduced in great detail, and the book also contains a full account of his work in astronomy and of the foundation of the new sciences, Cosmogony and Geogony. The author describes him as occupying easily the first place among living natural philosophers since the death of Poincaré and of Sir George Darwin in 1912, and regards his talents and achievements as quite unprecedented in the world's history. The book contains full reports of many of the addresses and lectures delivered by Prof. See and is copiously illustrated.

La Soudure Autogène. ("Autogeneous Welding"). Paris: Librairie du Mois Scientifique et Industriel. 1913. (2 fr. 75).

METHODS of autogeneous welding have come much to the fore in recent years, and the subject is one of which all up-to-date engineers and mechanics should have some knowledge. There are many different methods of welding to choose from, and this book is intended to provide a means of ascertaining which is preferable in given circumstances. The principles of autogeneous welding are explained in it clearly and impartially, and the advantages and disadvantages of the different processes are fully pointed out. In addition practical details concerning the handling of the necessary apparatus are also given, and some information as to the cost of different processes.

Notions Fondamentals de Chimie Organique. ("Fundamental Theories of Organic Chemistry"). By CHARLES MOUREU. Fourth Edition. Paris: Gauthier-Villars. 1913.

IN this book a summary is given of the main theories of organic chemistry, and matters of detail are omitted except in so far as the consideration of them is necessary for the understanding of the theoretical conceptions. The fourth edition has been carefully revised, and additional space is given in it to catalytic reactions and to methods of synthesis based upon the use of organo-metallic compounds. Important reactions brought about by light and the ultraviolet rays are described, and in stereo-chemistry active compounds containing no asymmetrical atoms are discussed, and also the transformation of an active substance into its optical antipode.

Die Quantitativen Untersuchungsmethoden des Molybdäns, Vanadiums, und Wolframs. ("Quantitative Methods of Estimating Molybdenum, Vanadium, and Tungsten"). By Dr. HANS MENNICKE. Berlin: M. Krayn. 1913. (Mk. 8).

THE metals molybdenum, vanadium, and tungsten and their alloys and compounds have recently greatly increased in importance from an industrial point of view, and a book devoted exclusively to the consideration of methods of detecting, estimating, and separating them is sure of a good reception. The author of this book has collected his material from all sources and has carefully sifted it. In many cases he has personally tested the methods described, and notes are frequently added as to the accuracy or rapidity of a method, while slight modifications are sometimes suggested. References are given to original literature, and all experimental details are fully stated. Most of the methods described are gravimetric or volumetric, very little space being given to colorimetric or electrolytic methods which cannot be relied upon for accuracy, and hence are not usually employed.

Physical Society.—The first Guthrie Lecture will be delivered by Prof. R. W. Wood (of Johns Hopkins University, Baltimore), at the Imperial College of Science, Imperial Institute Road, South Kensington), on Friday, February 27, 1914, at 8.30 p.m. The subject of the lecture will be "Radiation of Gas Molecules Excited by Light."

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clvii., No. 26, December 29, 1913.

Contributions to the Study of Benzhydrol. Preparation of Symmetrical Tetraphenylethane.—Pau Sabatier and M. Murat.—Diphenylcarbinol or benzhydrol, $C_6H_5.CHOH.C_6H_5$, can be obtained by reducing with sodium benzophenone dissolved in amyl alcohol, but attempts to prepare it by Grignard's reaction failed, the chief products being benzophenone, diphenylmethane, and symmetrical tetraphenylmethane. Tetraphenylethane can be obtained by the hydrogenation of benzophenone, benzyhydrol, or its oxide. The hydrogenation of tetraphenylethane gives diphenylmethane and dicyclohexylmethane. Thus the destruction of the organomagnesium complex gives, instead of benzhydrol, a product of dehydrogenation, benzophenone, and at the same time the products of hydrogenation diphenylmethane and symmetrical tetraphenylethane. The reaction of benzophenone with some mixed aliphatic organomagnesium compounds is analogous. Apparently the nascent benzhydrol is destroyed according to the equations:—

$$3C_6H_5.CHOH.C_6H_5 = 2H_2O + C_6H_5.CO.C_6H_5 + (C_6H_5)_2.CH.CH.(C_6H_5)_2,$$

and—

$$2C_6H_5.CHOH.C_6H_5 = H_2O + C_6H_5COC_6H_5 + C_6H_5.CH_2.C_6H_5.$$

Transformations of Chromic Fluosilicate. Fluopentaquochromic Fluosilicate.—A. Recoura.—Chromic fluosilicate, $(SiF_4)_3Cr_2F_6$, unlike the ferric salt, does exist, although in solution it is very rapidly converted into a green compound of formula $SiF_6.CrF.5H_2O$. This substance is fluopentaquochromic fluosilicate, corresponding to Jörgensen's two fluosilicates. It is perfectly stable in the desiccator, even *in vacuo*, but loses silicon fluoride when exposed to air, at first rapidly and then gradually more slowly, being finally transformed into a green fluoride of chromium of composition $Cr_2F_6.7H_2O$.

Determination of Chromium by Oxidation in Alkaline Medium.—F. Bourion and A. Sénéchal.—To determine chromium, soda is added to the chromic salt until the oxide formed is just dissolved and the solution is oxidised by means of hydrogen peroxide, the excess of which is decomposed by heating. The chromic acid is then reduced in a sulphuric solution by a known quantity of ferrous sulphate, the excess of which is determined with potassium permanganate. The chromium is obtained by difference. The authors find that this method gives accurate results when the chromium is alone or accompanied by iron. The destruction of the excess of hydrogen peroxide is greatly facilitated by the presence of sodium sulphate. The method fails in presence of nickel, cobalt, and manganese.

Vol. clviii., No. 1, January 5, 1914.

Ferrous Sulphate and its Hydrates.—R. de Forcrand.—Ordinary green vitriol always retains a certain amount of mother-liquor, which may be removed by powdering it and pressing between absorbent paper. Thus a powder of composition exactly corresponding to $SO_4Fe + 7H_2O$ may be obtained. It is absolutely stable in air at 15°, and does not either oxidise, effloresce, or deliquesce. When kept over sulphuric acid at the ordinary temperature and pressure for three days it yields the tetrahydrate. The dehydration of either of these hydrates at 100° gives the monohydrate. The preparation of the anhydrous salt is much more difficult, and the author believes that it has never yet been obtained in a pure state.

The monohydrate begins to lose water at 180° in a current of dry hydrogen, but the process is very slow. To effect complete dehydration within a reasonable time the temperature must be raised to 250°, but at that temperature a little basic salt is formed. The author has obtained the following values for the heats of solution at 13·5°:— $FeSO_4.7H_2O$, −4·323 cals; $FeSO_4.4H_2O$, +1·599 cals.; $FeSO_4.H_2O$, +7·538 cals.; $FeSO_4$, +14·901, cals.

Researches on Cadmium.—Manuel Veres.—When a fifth of its weight of cadmium sulphate is added to fused ammonium bisulphate at 300° a deposit of $2CdSO_4.Am_2SO_4$ is obtained. This salt, which has not been described before, is very soluble in water, and when its solution is slowly evaporated monoclinic crystals of $CdSO_4.Am_2SO_4.6H_2O$ separate. $2Cd_2SO_4.Am_2SO_4$ is attacked by concentrated H_2SO_4 at 100°, anhydrous $CdSO_4$ being left as the residue.

Bulletin de la Société Chimique de France.
Vol. xiii.-xiv., No. 24, 1913.

Preparation of Allyl Alcohol.—A. Kochler.—To prepare allyl alcohol heat 100 grms. of glycerin for one hour with 80 grms. of formic acid, and separate by distillation into three fractions:—(i.) The liquid coming over below 200°; (ii.) that passing over between 200° and 250—260°; (iii.) the residue. Determine the saponification index of (ii.). Add twice the corresponding quantity of solid potash, boil for an hour, and allow to cool. Decant off the upper layer, and dry by boiling with half its weight of dry potassium carbonate for four hours. The yield of allyl alcohol amounts to 32 per cent. Monoformine is the intermediate product.

Decomposition of Benzylidene-phenylisoxazolone by Phenyl Hydrazine.—André Meyer.—When equimolecular quantities of benzylidene-phenylisoxazolone and phenylhydrazine are boiled with alcohol the isoxazolone dissolves, and on dilution with water a colourless compound is precipitated. This is benzylidene phenylhydrazone. The mother-liquor yields on evaporation a small quantity of a substance the properties of which recall those of the phenylisoxazolone, and also uncrystallisable substances which have not been identified. Thus phenylhydrazine splits up the molecule at the double bond. Hydroxylamine and bases capable of combining with aldehydes and ketones behave similarly.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xlvi., No. 16, 1913.

Methylation of Metals by Action of Aluminium Carbide on Dissolved Salts.—Siegfried Hilpert and Martin Ditmar.—When aluminium carbide is introduced into a hydrochloric acid solution of sublimate, mercury methyl chloride is formed; in a neutral or faintly acid solution mercury dimethyl results. Bismuth trimethyl can be synthesised in the same way. Tin salts can also be methylated by means of aluminium carbide, and the formation of the methyl tin derivatives, which are readily detected by their strong characteristic smell, can be employed as a test for the metal. Probably like water or hydrochloric acid mercury chloride can bring about the decomposition of aluminium carbide. The negative chlorine combines with the aluminium, while the monovalent radicle $HgCl$, with three of the hydrogen atoms coming from the water or the hydrochloric acid, combines with the carbon.

MISCELLANEOUS.

Royal Institution.—On Saturday next, February 28, at 3 o'clock, Prof. Sir J. J. Thomson begins a course of six lectures on "Recent Discoveries in Physical Science." On Tuesday, March 3, Prof. Sir J. H. Biles delivers the first of three lectures on "Modern Ships—(1) Smooth Water Sailing; (2) Ocean Travel; (3) The War Navy." On Thursday, March 5, Prof. C. F. Jenkin begins a course of three lectures on "Heat and Cold." The Friday Evening Discourse on February 27 will be delivered by Prof. W. A. Bone on "Surface Combustion," and on March 6 by Canon Hannay (George A. Birmingham), on "The Stage Irishman."

Anglo-American Exposition (May to October), 1914.—The Photography Committee of the Anglo-American Exposition, 1914, is anxious to make this Section as widely known as possible—especially amongst manufacturers. The Exposition will afford a unique opportunity of bringing British industries to the notice of visitors from all parts of the world. From the communications that have been received from the United States Office there appears to be no doubt that the Exposition will be warmly supported by American exhibitors and the Government of the United States, and will be visited by large numbers of Americans. It is the desire of the British Committee that the Photography Section shall be the most extensive ever brought together and worthy of the British Empire. *Liberal Arts Sub-committee (Photography)*—E. Sanger-Shepherd (Chairman); Chapman Jones, F.I.C. (Vice-Chairman); Sir William Abney, K.C.B., F.R.S.; Charles F. Butler, A.R.C.Sc., F.R.P.S., F.R.A.S.; F. Martin Duncan, F.R.M.S., F.R.P.S.; Dr. R. T. Jupp, M.B., B.Sc., F.R.C.S.; Prof. R. Meldola, D.Sc., LL.D., F.R.S.; Frank F. Renwick, A.C.G.I., F.C.S., F.R.P.S.; Sir Philip Watts, K.C.B., LL.D., F.R.S., D.Sc.; Sir Henry Trueman Wood; Sir J. Benjamin Stone, J.P., F.S.A., F.S.S.; Charles Urban, F.Z.S. *Classification*—Raw materials, instruments, and apparatus of photography; materials for photographic studies; positive and negative photography on glass, paper, woodstuffs, enamel, &c.; photogravure, photo-collotypes, photo-lithography, stereoscopic proofs; photographic enlargements and reductions; colour photography; natural and artificial colour printing; cinematography, apparatus, and processes.

MEETINGS FOR THE WEEK.

Monday, 23rd.—Royal Society of Arts, 8. (Cantor Lecture). "Artistic Lithography," by Joseph Pennell.

Tuesday, 24th.—Royal Institution, 3. "Animals and Plants under Domestication," by Prof. W. Bateson, F.R.S., &c.

Wednesday, 25th.—Royal Society of Arts, 8. "Rural Housing," by T. Brice Phillips.

Thursday, 26th.—Royal Institution, 3. "Hamlet in Legend and Drama," by Prof. I. Gollancz, Litt.D.

— Royal Society. "Diffraction of Light by Spheres of Small Relative Index," by Lord Rayleigh. Studies of the Properties Operative in Solutions—XXXI., Sulphonic Acids and Sulphuric Acid as Hydrolytic Agents—a Discussion of the Constitution of Sulphuric and other Polybasic Acids and of the Nature of Acids; XXXII., The Influence of Sulphonates on the Hydrolytic Activity of Sulphonic Acids—a Contribution to the Discussion on the Influence of Neutral Salts," by H. E. Armstrong and F. P. Worley. "Morphological Studies of Benzene Derivatives—V., The Correlation of Crystalline Form with Molecular Structure, a Verification of the Barlow-Pope Conception of 'Valency Volume,'" by H. E. Armstrong, R. T. Colgate, and E. H. Rodd. "Magnetic Properties of Iron when shielded from the Earth's Magnetism," by E. Wilson. "Occurrence of Ozone in the Upper Atmosphere," by J. N. Pring. "Meteoric Iron from Winburg, Orange Free State," and "Electrification produced during the Raising of a Cloud of Dust," by W. A. D. Rudge. Electrical Ignition of Gaseous Mixtures," by W. M. Thornton.

Friday, 27th.—Royal Institution, 9. "Surface Combustion," by Prof. W. A. Bone, F.R.S.

— Physical, 8.30. (At the Imperial College of Science, South Kensington). "Radiation of Gas Molecules Excited by Light," by Prof. R. W. Wood.

— Swedenborg Society, 8.15. (At 1, Bloomsbury Street). "The Body and the Soul in Swedenborg's Philosophy," by L. de Beaumont-Klein, D.Sc.

Saturday, 28th.—Royal Institution, 3. "Recent Discoveries in Physical Science," by Prof. Sir J. J. Thomson O.M., F.R.S.

THE CHEMICAL NEWS.

Vol. CIX., No. 2831.

NOTES ON THE EFFECT OF TUNGSTEN ON THE AMMONIUM-MOLYBDATE ASSAY FOR LEAD.

By HERBERT LAVERS.

At a previous meeting of the Broken Hill Branch of the Institute the writer reported the occurrence of two minerals in the sulphide zone of Block 14 Mine, both of them new to Broken Hill. They were wolfram and scheelite. The former—wolfram—a tungstate of iron and manganese, gave on assay 42 per cent tungstic acid. The latter—scheelite—a tungstate of lime, gave 35 per cent tungstic acid. Both these samples contained zinc and lead sulphides, and clean specimens of wolfram gave 64 per cent WO_3; scheelite gave 70 per cent WO_3.

An estimation of the lead in these samples revealed the fact that the presence of tungsten in the ore seriously interfered with the ammonium-molybdate assay for lead, giving low results according to the amount of tungsten present in the ore. The sample under review, when assayed under ordinary conditions, gave a negative value for lead, but on removal of the tungsten showed 9·8 per cent Pb. The reason for this interference is shown on an examination of the reactions which occur in the assay. The ore is reduced with suitable acids, and the lead obtained in the form of sulphate, which is dissolved in ammonium acetate, thus:—

$$\text{A. } \underset{\text{Lead sulphate.}}{PbSO_4} + \underset{\text{Ammon. acetate.}}{2NH_4C_2H_3O_2} = \underset{\text{Lead acetate.}}{Pb(C_2H_3O_2)_2} + \underset{\text{Ammon. sulphate.}}{(NH_4)_2SO_4}$$

The lead acetate thus formed is now titrated with a standard solution of ammonium molybdate as follows:—

$$\text{B. } \underset{\text{Lead acetate.}}{Pb(C_2H_3O_2)_2} + \underset{\text{Ammon. molybdate.}}{(NH_4)_2MoO_4} = \underset{\text{Lead molybdate.}}{PbMoO_4} + \underset{\text{Ammon. acetate.}}{2NH_4C_2H_3O_2}$$

The above reactions take place under ordinary conditions, but when the ore contains tungsten, this is converted into the trioxide by the action of the acids, and during solution by ammonium acetate it readily combines with the lead, forming lead tungstate as per equation (C.)—

$$\text{C. } \underset{\text{Lead acetate.}}{Pb(C_2H_3O_2)_2} + \underset{\text{Ammon. tungstate.}}{(NH_4)_2WO_4} = \underset{\text{Lead tungstate.}}{PbWO_4} + \underset{\text{Ammon. acetate.}}{2NH_4C_2H_3O_2}$$

So that if sufficient tungsten be present in the ore to combine with all the lead present, the addition of the standard solution gives negative results.

It therefore becomes necessary to remove the tungsten before proceeding with the lead assay, and this is done in the following way:—

The ore is digested in 10 cc. HCl, 10 cc. HNO_3 added, and evaporated to small bulk. This is taken up with water, boiled, allowed to settle, and filtered. By this means the tungsten is converted into tungstic acid, and removed with the silica. To the filtrate is added H_2SO_4 taken to white fumes (this is important, otherwise gives 0·2 high in 14 per cent lead), and the assay proceeded with in the usual manner.

The reaction occurring in equation (C) suggested a rapid volumetric method for the estimation of tungsten.

The tungstic acid obtained on the filter-paper in the previous operation is dissolved in ammonium hydroxide, neutralised with acetic acid, and an excess of standardised solution of lead acetate added. This combines with the WO_3 to form lead tungstate as per equation (C). The excess of lead acetate solution is now titrated with ammonium molybdate solution, as in the ordinary lead assay, and shown by equation (B). From the formula $PbWO_4$ the factor for tungstic acid, WO_3, can be obtained.

The presence of tungstic acid has no effect on the zinc assay. A laboratory experiment in flotation was carried out on some sulphide ore containing scheelite in order to see if this method could be used in separation. The following results were obtained.

	Lead.	Silver.	Zinc.	WO_3.
No. 1 concentrate ..	52·4	23·4	13·2	—
Residue	2·8	15·6	1·0	20·4
No. 2 concentrate ..	53·6	26·2	12·6	—
Residue	3·5	14·2	1·0	17·4

Note the high silver in the residue, which latter readily lends itself to further concentration by tabling.

The above has a local interest from the fact that lead concentrate made from a parcel of Block 14 ore showed the presence of 5·5 per cent WO_3. The concentrate contained 63 per cent lead (approx.), and the assay value shown by buyer and seller differed by upwards of 3 per cent. The umpire, who evidently recognised and removed the tungsten, agreed with the higher of the two assays.

The method shown above for the elimination of the tungsten in the determination of the lead was embodied in an agreement for the purchase of crude ore from Block 14 Mine, and has also been adopted in the lead assay for the purchase of certain lead concentrates.—*Australasian Institute of Mining Engineers*, 1913, No. 10.

THE APPLICATION OF DIPHENYLCARBAZIDE AS INDICATOR IN THE TITRATION OF IRON WITH DICHROMATE.

By O. L. BARNEBEY and S. R. WILSON.

Brandt (*Zeit. Anal. Chem.*, xlv., 95, published in 1906, a method using diphenylcarbazide ("Beilstein," iv., 671), called by him "diphenycarbohydrazide," as an "inside indicator" for the titration of iron. Shortly after the publication of the article one of us tried the method as outlined by Brandt and by following his directions minutely could not obtain concordant results. A detailed study, however, developed an interesting and valuable modification of this method and likewise an application for the analysis of ores.

In 1900, Cazeneuve (*Bull. Soc. Chim.*, xxiii., 592, 701, 769) pointed out the fact that diphenycarbazide could be used to detect extremely small quantities of chromic acid, giving the sensitiveness as 1 : 1,000,000. Brandt carries the work further and uses this substance as an indicator for the titration of iron. He states that large amounts of hydrochloric acid and also manganese sulphate solution containing phosphoric acid must be present to prevent too rapid destruction of the indicator. His conditions for titration are—0·2 to 0·7 grm. of iron, 60 to 80 cc. dilute hydrochloric acid (sp. gr. 1·12), 100 cc. manganese sulphate solution (containing 6 kg. manganese sulphate), 33 litres dilute sulphuric acid (1 : 3), 3 litres phosphoric acid (sp. gr. 1·7) diluted to 60 litres,—diluted to a total volume of 1½ litres, and 5 cc. of a 0·1 per cent solution of indicator added. Smaller amounts than 0·2 grm. of iron may be titrated by slightly modifying the conditions.

The colour changes involved are very marked. The first drop of dichromate added gives a pink or red tinge, which becomes deep red as the titration proceeds. This colour gradually changes to lavender, which seems to be caused by the complementary nature of the red compound and trivalent chromium. The lavender fades out and finally the addition of one drop of the dichromate gives a sharp change to the clear green colour of chromic chloride.

Experimental.

The indicator was prepared by heating 20 grms. of urea with 200 cc. of phenylhydrazine, gradually raising the temperature from 150 to 170° for about four hours. The resulting product was dissolved in hot alcohol, re-crystallising by cooling, filtered, and washed with cold alcohol. The re-crystallisation was repeated three times. The crystalline product was nearly pure white, but had a tendency to gradually become pink when exposed to the air for some time. The melting-point was 163·5° ("Beilstein," *loc. cit.*). The colour tests outlined by Skinner and Ruheman (*Journ. Chem. Soc.*, liii., 551) were also tried with positive results. Solution was effected by dissolving the indicator in strong acetic acid and diluting to an appropriate volume. One grm. per litre is convenient.

A manganese sulphate solution was prepared by using the following proportions:—200 grms. of manganese sulphate, 1100 cc. of dilute sulphuric acid containing one part of acid (sp. gr. 1·84) and three of water, 100 cc. of phosphoric acid (sp. gr. 1·70) diluted to two litres.

Titrating 25 cc. portions of a 0·1 N solution of ferrous iron and varying amounts of indicator, manganese sulphate solution, and acid with 0·1 N dichromate solution required from 25·60 to 28·00 cc. of the latter. Using constant amounts of the iron, manganese sulphate solution, and acid, having the indicator only as variable, gave results of the same order. However, by using constant amounts of indicator, variable amounts of manganese sulphate solution, variable amounts of acid, and constant amounts of ferrous iron in a series of determinations practically the same quantity of dichromate was required in each titration.

Series I. of the table is a series of "blanks" obtained with an indicator solution (about 0·17 per cent indicator) without the presence of ferrous iron, and Series II. in the presence of a constant quantity of iron in the ferrous state. Series I. was obtained as follows:—To about 300 to 400 cc. of water 10 cc. of strong hydrochloric acid, 10 cc. of manganese sulphate solution, and a measured amount of indicator solution are added followed by 3 cc. of 10 per cent ferric chloride solution, and the indicator titrated slowly with tenth normal dichromate, agitating very vigorously after the addition of each drop. The disappearance of the red and appearance of a pale green tint marks the end point. From three to five minutes must be taken for the titration to avoid overrunning the end. Series II. varies from Series I. only in the use of constant quantities of 0·1 N ferrous iron and the use of 0·1667 N dichromate solution.

A glance at these figures shows at once that the indicator itself is the cause for the variable results, the larger the amount of indicator used the more dichromate is necessary to complete the titration. A regular increase in quantity of dichromate is noticed in both series as the amount of indicator becomes larger. In Series II. the value of 6 cc. of the oxidising agent is closely approached in each titration if in each case the dichromate equivalent to the amount of indicator used is subtracted; thus, 5 cc. of the indicator required 0·86 cc. of dichromate with no ferrous iron present. Hence, if the value of this blank is subtracted from the value found with 10 cc. of ferrous iron and 5 cc. of indicator present, 6 cc. in one case and 6·04 cc. in the other is found to be the actual volume of oxidising solution required. Brandt says nothing about this factor; in fact he even states that the quantity of indicator may be doubled and still have no appreciable effect on the titration. Although the titrations were made in a smaller volume than those of Brandt, yet using the dilution he recommends his results could not be confirmed. The work above suggested a direct ratio existing between oxidising agent and indicator.

To test this ratio more rigidly an exactly 0·1 per cent solution of the indicator was prepared and 10 cc. of this solution titrated with a solution of dichromate containing 0·00438 grm. per cc., the latter being standardised against

SERIES I.

HCl. Cc.	Indicator. Cc.	Manganese solution. Cc.	$FeCl_3$. Cc.	0·1/N $K_2Cr_2O_7$. Cc.
10	0·5	10	3	0·14
10	0·5	10	3	0·18
10	1·0	10	3	0·30
10	1·0	10	3	0·32
10	2·0	10	3	0·60
10	2·0	10	3	0·60
10	3·0	10	3	0·92
10	3·0	10	3	0·96
10	4·0	10	3	1·22
10	4·0	10	3	1·20
10	5·0	10	3	1·42
10	5·0	10	3	1·42
10	10·0	10	3	2·76
10	10·0	10	3	2·74
10	15·0	10	3	4·18
10	15·0	10	3	4·26

SERIES II.

(10 cc. of ferrous iron solution are equivalent to 6 cc. of dichromate solution).

0·1 N ferrous iron solution. Cc.	HCl. Cc.	Manganese solution. Cc.	Indicator. Cc.	$FeCl_3$. Cc.	0·1667 N $K_2Cr_2O_7$. Cc.
10	10	10	2	3	6·36
10	10	10	2	3	6·36
10	10	10	5	3	6·90
10	10	10	5	3	6·86
10	10	10	10	3	7·62
10	10	10	10	3	7·66
10	10	10	15	3	8·46
10	10	10	15	3	8·48
None	10	10	5	3	0·86

pure ferrous ammonium sulphate, using ferricyanide as indicator on a spot plate. One and eight-tenths cc. of the dichromate, or 0·0079 grm., were required for the titration. Using the proportion:—

Wt. of indicator.		Weight of dichromate.		Mol. wt. of indicator.		Mol. wt. of dichromate.
0·01	:	0·0079	::	x	:	294

$$x = 370.$$

However, the molecular weight of the indicator is 242; hence, the number of molecules reacting would be $370 \div 242 = 1·5$ for each molecule of dichromate, and the reaction would probably be—

$$3C_{13}H_{14}N_4O + 2K_2Cr_2O_7 + 16HCl = $$
$$= 4CrCl_3 + 4KCl + 3C_{13}H_{10}N_4O + 14H_2O.$$

This equation is advanced for the lack of a better one at the present time. On the basis of three molecules of indicator being equivalent to two molecules of dichromate the following ratio holds:—3 mols. $C_{13}H_{14}N_4O$ (726) : 2 mols. $K_2Cr_2O_7$ (588) :: Wt. of indicator : Wt. of dichromate. Weighing out exactly 0·01 grm. of indicator and using 0·02 N potassium dichromate solution required 8·24 cc., or 0·00807 grm. of the latter. Theoretically calculating 0·01 grm. of the indicator according to the above proportion gives 0·00809 grm. of dichromate. In all likelihood side reactions may occur under some conditions of titration, in which cases the agreement may not be so close to the theoretical.

This process was repeated, using permanganate instead of dichromate, and the theoretical ratio of five molecules of indicator to four of $KMnO_4$ verified by experiment. A standard solution of chlorine water was likewise used and the ratio of two molecules of Cl_2 to one of indicator found to exist.

Analysis of Iron Ores.

We find that this method of determining iron can be readily applied to the analysis of iron ores. A 0·5 grm. (larger if the ore is of low grade) sample is weighed into a number two beaker. Pour over the sample 15 to 33 cc. of hydrochloric acid (sp. gr. 1·2), heat just below boiling, adding sufficient stannous chloride (280 grms. of $SnCl_2.2H_2O$ and 150 cc. of hydrochloric acid, sp. gr. 1·20, per litre) to reduce most of the iron as it dissolves yet leaving a distinct yellow tinge in the solution when the solvent action has ceased.

If a dark residue remains, filter, wash free from hydrochloric acid, and ignite the filter paper in a platinum crucible. Add a small quantity of sodium carbonate to ash, heat to quiet fusion. Cool, place crucible in a small beaker, and dissolve the melt in a small portion of boiling water. Add solution and precipitate, if any, to the hydrochloric acid extraction.

Heat the solution to boiling, wash off the cover and the sides of the beaker with a small portion of water (the volume should not be over 30 to 40 cc.), and add stannous chloride drop by drop to the hot solution until one drop will give a colourless solution, then add one drop in excess. (If a larger excess of stannous chloride has been added, add potassium permanganate until a permanent yellow colour appears, then reduce as above.) Transfer to a litre beaker, dilute to about 500 or 600 cc., add 30 cc. of mercuric chloride (saturated solution), stir vigorously for a moment, then add 20 cc. of manganese sulphate solution followed by 10 cc. of concentrated hydrochloric acid and an exact volume (2 to 3 cc.) of the indicator. Titrate with standard dichromate. The first few drops added will cause an intense red colour to appear. This colour changes to a purple as the titration proceeds, and as the end-point is approached it gradually fades, finally giving the sharp change to the chromic chloride. This gradual change minimises the danger of overtitration and allows the titration to proceed rapidly. The burette reading is now taken. The dichromate value of the indicator is obtained by titrating the same volume of the indicator as was employed previously under the same conditions as those of an actual analysis, except that 3 cc. of a 5 per cent solution of ferric chloride are added preceding titration. The blank titration must be performed very slowly to avoid overtitration. Another method used to check the reducing value of the indicator solutions consisted in starting with a definite amount of ferrous iron in solution, adding the usual amounts of manganese sulphate, acid, and 2 cc. of indicator, then titrating. Utilising the same amounts of ferrous iron, acid, manganese sulphate, and 4 cc. of indicator, again titrate. The difference between the two readings gives the reducing value of 2 cc. of the diphenylcarbazide. This scheme of titration of the blank allows a more rapid titration. Subtract the volume required for the blank from the original volume of dichromate and calculate the per cent of iron in the sample.

Series III. contains the results obtained with four iron ore samples from the Lake Superior region. The "per cent iron" column in each case contains the per cent of iron obtained by the permanganate method.

Several series of analyses, some with very small, others with larger amounts of iron, were made with results which check closely. With very small quantities of iron it is better to use a smaller quantity of indicator than with high iron content, adding some ferric chloride as in the blank determination. Titration of small amounts of iron should be made slowly with thorough agitation of the solution.

A solution of the indicator has a tendency to decompose slowly when exposed to the air because of oxidation, hence solutions should be kept in well-stoppered bottles. Under ordinary laboratory conditions a solution should be prepared fresh every few days unless protected from the action of the air. We have kept indicator solutions several months in an atmosphere of carbon dioxide without appreciable decomposition. However, the only apparent difference is a lowering of the reducing power and a corresponding less intense colouration during titration, hence a larger amount of the partially oxidised indicator is necessary to give the same effect as a fresh or protected solution. Series IV. contains the tabulated results of a number of blanks titrated with a constant amount of indicator which has been exposed to the air in a bottle with the stopper removed. This is a portion of the same indicator solution employed several days previous in Series I. and II.

SERIES III.—*Iron Ores.*

No.	Per cent Iron.	Per cent found.	Deviation.
1.	64·84	64·77	0·07
2.	64·84	64·85	0·01
3.	64·84	64·75	0·09
4.	64·84	64·71	0·13
5.	64·84	64·74	0·10
6.	64·84	64·75	0·09
7.	64·84	64·76	0·08
8.	64·84	64·95	0·11
9.	64·84	64·70	0·14
10.	64·84	64·72	0·12
11.	64·84	64·79	0·05
1.	62·33	62·47	0·14
2.	62·33	62·39	0·06
3.	62·33	62·52	0·19
1.	66·29	66·48	0·19
2.	66·29	66·38	0·09
3.	66·29	66·65	0·36*
4.	66·29	66·29	0·00
5.	66·29	66·34	0·05
1.	28·15	28·19	0·04
2.	28·15	28·24	0·09
3.	28·15	28·20	0·05

* The cause for this particularly high result was not known at the time of titration.

SERIES IV.

HCl. Cc.	Manganese solution. Cc.	Indicator. Cc.	$FeCl_3$. Cc.	0·1/N $K_2Cr_2O_7$. Cc.
20	10	5	0·16	1·10
20	10	5	0·50	1·02
20	10	5	1·00	1·00
20	10	5	5·00	0·96
20	10	5	10·00	1·04

Conclusions.

1. The end-point is an excellent one.
2. The indicator is a reducing agent and is oxidised by the dichromate during the process of titration. A blank determination must be made to ascertain this reducing power.
3. With the above modification the method is applicable to the analysis of ores for their iron content.
4. Small amounts of iron can be determined within the accuracy of the other methods in common practice.
5. In all likelihood the principle involved can be utilised in a number of other analyses. This point is being investigated.

The oxygen ratio existing between the oxidising agent and the indicator as obtained by different methods, the chemical reaction involved in causing the colour change titration, and the use of other compounds similar to diphenylcarbazide, especially those containing double bonds between the nitrogen atoms, are being likewise investigated.

We desire to express our appreciation to Dr. Benton Dales for his interest in the work throughout this investigation.—*Journal of the American Chemical Society*, xxxv., No. 2.

THE SCIENTIFIC WEEK.

(From Our Own Paris Correspondent).

THE WORLD'S PRODUCTION OF PETROLEUM IN 1913.

According to statistics that have been published for the first three quarters of the year 1913 concerning the exploitation of the different petroliferous regions of the whole world, it is seen that all the records established hitherto have been beaten. A comparative statistic of the last five years shows that the world's production has gone on steadily increasing. In 1912, the countries producing petroleum supplied 351,178,236 barrels of 42 gallons each, which makes 2,190,383 waggons of petroleum of 10,000 litres each. The increase which the petroliferous production of 1913 will show will certainly be due to the formidable gain registered by the output of California and of the naphtha fields of Kansas and Oklahoma. It is the United States that holds the first place among the countries producing petroleum. Their annual production exceeds 220 millions of barrels, and is 64 per cent of the whole world's production. Russia comes next, with 70 millions of barrels and a percentage of 19·37. These two countries alone represent, then, about 82 per cent of the petroliferous production of the whole world. The third place is held by Mexico, a country that has only just lately come to the front as a producer of petroleum. The part it contributes is 4·71 per cent. Roumania and the Dutch Indies are closely matched for the fourth and fifth places, with a rate of 3·70 per cent and 3·09 per cent in the naphthiferous production of the world. Still another country on which geologists found great hopes for the future in what concerns petroleum is the Argentine Republic, the naphtha beds of which have up till the present time been very little explored.

A VOTING MACHINE.

The secret of votes is one of the most difficult things to obtain. The isolators that are to be brought into use at the next general legislative elections, and that were tried quite recently at Ivry sur Seine, near Paris, are very imperfect when they are compared with the automatic electoral machine devised by an engineer, M. Stefan Russo. The advantages of this new machine are numerous. It assures the secret of the vote even in the middle of a public square; it suppresses the voting ticket that permits cheating; it likewise suppresses the counting of the votes, often very long and the cause of numerous quarrels; it also permits the illiterate to vote; it obliges the elector to perform his duty as a citizen; it regulates the electoral operations automatically. Lastly, it is extraordinarily rapid, since 10,000 voters were able to vote in less than six hours, including the counting of the votes. The electoral cabin has one single door, over which is a register counting the number of electors who cross the threshold. Several lists are placed in the inside of the cabin, according to the number of political parties that are represented at the election. Every list mentions the party to which it is attributed; conservatives, liberals, radicals, socialists, and a special sign for each of them, destined for the illiterate. Above each slip, into which must be pressed a knob that has the form of a cylinder, are placed the photographs of the candidates and their names. To vote the elector must press on one of the knobs, which will only return to its primitive position when once the door of the cabin is open. So it is quite impossible to vote twice for the same candidate. Then, again, the door of the cabin can only be opened if the elector has completely fulfilled his electoral duty, which he cannot refrain from doing when once he has entered the cabin. If he has to vote for three deputies or five municipal councillors, the apparatus regulated for three or five obliges him to vote three or five times. At the same time, M. Russo's machine does not allow of voting for more candidates than is required. When the voting is ended, the president can immediately know the results of the polling. By means of a key he raises the plate bearing the photographs of the candidates. Underneath another slab appears bearing the same photographs with below each of them the number of votes obtained by the different candidates. The counting of the votes is thus ended. The electoral machine can be easily applied to all sorts of combinations. A regulating system enables the apparatus to be easily regulated to vote for a variable number of seats. It would even be quite easy to adapt the machine to vote for the proportional representation.

THE LIMIT OF FATIGUE.

Professional fatigue can be measured from the variations of the tracing or sketch of the movements of the heart. According to the experiments of M. Jules Amar explained by Prof. Dastre, it has been seen that as the power developed by the muscles increases the form of the cardiograms is changed. Their summit becomes more and more pointed. The undulation on the right that is supplied by the contraction of the heart lowers progressively. After the contraction that drives back the blood an aspiration is produced, the value of which goes on increasing. In all works of strength, carrying of burdens up staircases, fatiguing walking, running, work with the hammer, M. Amar has noticed curves that have an aspect identical to the physiological limit of fatigue.

THE FISH OF MADAGASCAR.

M. Edmond Perrier, Director of the Paris Natural History Museum, in the name of M. Pellegrin, Professor of the Museum, has presented a paper concerning the fresh water fish of Madagascar. M. Pellegrin has especially studied the *atherinides*, alimentary fish, of great economical importance for the large African Island. These fish came from the sea and have gradually become acclimatised in the fresh water of the rivers and lakes.

THE RETURN TO THE TYPE.

The question of naturalised foreigners is one that for some considerable time past has been preoccupying our sociologists. In a country like France, in which the birth rate is decreasing or at least stationary, it seemed to some that there would be a danger for the race in the penetration into the national territory of a large number of individuals natives of other countries. The danger, however, would not exist and would doubtless be transformed into a benefit if these foreigners intermarried with our compatriots. M. J. Lammonier, indeed, showed at the last meeting of the French Eugenic Society that the children from these mixed unions "resemble more the parent, whatever the sex may be, in whose original country they are born and live, rather than the other one." In other words, human half-breeds return with great rapidity to the ancestral type represented by the ascendants who lived in the country in which the half-bred or mongrel race was born. From this it results that foreigners married in France and living in this country have a posterity which becomes Frenchified without delay and definitely. Thus, by favouring the marriage and establishment of desirable, that is to say, healthy foreigners, according to the data of Dr. Lammonier, we might hope to palliate in a certain measure the threatening depopulation. Before the great difficulty of finding efficacious and applicable means for this end it would doubtless be well not to neglect this unexpected remedy.

Royal Institution.—On Tuesday next, March 3, at 3 o'clock, Sir John H. Biles begins a course of lectures on "Modern Ships—(1) Smooth Water Sailing; (2) Ocean Travel; (3) The War Navy; and on Thursday, March 5, Prof. C. F. Jenkin delivers the first of three lectures on "Heat and Cold—Modern Applications, Theory of Caloric, Heat Engines, Freezing Machines, &c." The Friday Evening Discourse on March 13 will be delivered by Sir Walter R. Lawrence on "An Indian State"; and on March 20, by Lord Rayleigh on "Fluid Motions."

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, February 12, 1914.

Sir William Crookes, O.M., President, in the Chair.

Papers were read as follows:—

"*Chemical Action that is Stimulated by Alternating Currents.*" By S. G. Brown.

This paper describes experiments on the effects produced by passing a rapid alternating current through simple voltaic cells, the general effect being to stimulate chemical action and to cause the cells to give a greater supply of continuous current which otherwise could not be produced.

The alternating current will prevent a cell from polarising, or, if the exposure of the zinc anode is small, and the continuous current delivery restricted by this means, will increase the current by stimulating a greater chemical action between this pole and the electrolyte.

This latter action depends greatly upon the alternating current density, and if this is sufficiently high the chemical action induced may be sufficiently intense to oxidise any known metal forming the anode.

It is thought that this phenomenon is one of wide application and may explain the working of the Branley coherer.

"*Effect of the Gangetic Alluvium on the Plumb-line in Northern India.*" By R. D. Oldham, F.R.S.

The depression occupied by the Gangetic alluvium along the southern face of the Himalayas, as determined by geological observation, has a nearly vertical face on the north, and a floor sloping upwards in a southerly direction to the surface. The depth at the northern margin is from 15,000 to 20,000 feet, and the width of the effective depression ranges up to about 200 miles: the density of the material filling this trough is not far from an average value of 2·1, that of the rocks forming the Himalayan range and the floor of the trough being about 2·7. The effect of the defect of mass in the Gangetic depression is calculated and shown to be capable of producing about 30″ of northerly deflection of the plumb-line at the margin of the range, a deflexion which drops rapidly on either side of the margin but more rapidly to the south than the north At 20 to 30 miles south, the distance depending on the width of the trough, it becomes zero, and at greater distances is replaced by a southerly deflexion.

It is shown that the deflexions so produced agree very closely with the residuals, or deflexions not accounted for by the visible topography, as calculated by Major H. L. Crosthwait for stations near or south of the Himalayan boundary. At stations to the north the data for comparison are not available.

"*Note on the Origin of Black Body Radiation.*" By G. W. Walker, F.R.S.

This is a supplement to my paper on the same subject, recently communicated to the society, in which I showed that an empirical radiation function—

$$k\theta^5\left(\frac{\lambda\theta}{\lambda^2\theta^2+n^2}\right)^4$$

gave an exceedingly good representation of the experimental data.

It is now shown that arbitrary disturbances, all of the type te^{-n_0t}, lead by Fourier resolution to precisely the above form of energy distribution.

This form of disturbance may be interpreted as a solution of the equation—

$$\ddot{x}+2n_0\dot{x}+n_0^2x=0$$

which represents the motion of a strictly aperiodic dynamical system.

"*Transmission of Electric Waves along the Earth's Surface.*" By Prof. H. M. Macdonald, F.R.S.

A series is obtained which represents the magnetic force at any point on the surface when the oscillator is also on the surface; the series converges rapidly for large values of θ, and for not very large values the first term is a sufficient approximation. For small values of θ the series converges very slowly. Tables showing the form in amplitude with increase of distances have been calculated for different wave-lengths.

"*Transparence or Translucence of the Surface Film produced in Polishing Metals.*" By G. T. Beilby, F.R.S.

Earlier observations on translucence in these fims are confirmed by the further study of the film on polished copper. Minute pits caused by gas bubbles in the metal are shown to be covered by a translucent blue film through which rays of light reflected from the concave surface of the pit are seen as red spots. By the action of a solvent the film covering the pits can be completely removed, or it can, if desired, be so reduced in thickness that it becomes perfectly transparent. In either case the whole inner surface of the pit can be seen distinctly.

"*A Thermomagnetic Study of the Eutectoid Transition Point of Carbon Steels.*" By S. W. J. Smith, D.Sc., and J. Guild.

The magnetic properties of steel at temperatures near the eutectoid transition point (A1) seemed to deserve further examination. Simultaneous observations of intensity of magnetisation and of temperature were made over various ranges of heating and of cooling in different magnetic fields. Nine steels containing percentages of carbon ranging between 0·1 and 1·5 were used. Each steel contained about 0·2 per cent, or less, of silicon and of manganese.

It was found that the temperature corresponding with the beginning of the transformation of the eutectoid during heating (Ac1) could be fixed within ± 1° C. under suitable conditions. This temperature was 735° C. as read by our thermometers, which however were better adapted for comparative measurements than for determination of absolute values. It was the same for all the steels.

The reasons why this temperature, although constant, must be higher than the true equilibrium temperature are discussed. The existence of the lag and of its causes is also shown by direct experiment. A thermomagnetic method of estimating the true equilibrium temperature is described and used.

The inverse change from solid solution to eutectoid during cooling (Ar1) is also clearly shown upon all the thermomagnetic curves. The conditions under which the eutectoid separates are, however, seen to be more complex than those under which it disappears. The temperature of the change is no longer constant. It is highest in the hypo-eutectoid steels, and it diminishes continuously in the hypo-eutectoid steels with the percentage of carbon. The range is from about 725° to about 695° C.

The cause of this phenomenon is discussed.

"*Note on Osmotic Pressure.*" By W. R. Bousfield, M.A.

The osmotic pressure of a solution is the pressure under which the internal vapour pressure of the solution is raised to equality with the vapour pressure of the pure solvent. It is the compression of the solution which raises its internal vapour pressure. It is shown that the assumption that the molecular interspaces of a solution are filled with vapour, which there behaves as a perfect gas, leads to the same general relation between vapour pressure and osmotic pressure as is given by thermodynamical considerations. The anomalous fact that the osmotic pressure of a decinormal sucrose solution is found to be greater at 0° C. than at 5° C. is explained by reference to the constitution of water and the effect of compression upon the ice molecules.

CHEMICAL SOCIETY.

Ordinary Meeting, February 5, 1914.

Prof. W. H. Perkin, LL.D., F.R.S., President, in the Chair.

The President referred to the loss sustained by the Society, through death, of Mr. Frank Baker and Mr. Frederick George Richards.

Certificates were read for the first time in favour of Messrs. Abdel Hameed Ahmad, B.Sc., The University, Edgbaston, Birmingham; Charles Wesley Bayley, 63, Caxton Road, Wood Green, N.; Robert Barclay Craig, 50, North Albion Street, Glasgow; Jaroslav Heyrovsky, B.Sc., 24, Agincourt Road, N.W.; Lawson John Hudleston, B.Sc., 68, Parliament Hill, Hampstead, N.W.; Arthur Ulysses Newton, B.Sc., 37, Netherhall Gardens, Hampstead, N.W.; Lall Behary Seal, Third Assistant Chemical Examiner, Rangoon, Burma; Norman Cecil White, B.A., B.Sc., 35, Spencer Park, Wandsworth, S.W.

Of the following papers, those marked * were read:—

*25. "*Existence of Racemic Compounds in the Liquid State.*" By Clarence Smith.

The investigation, by the Ramsay-Shields' method, of the existence of racemic compounds in the liquid state (Mitchell and Smith, *Trans.*, 1913, ciii., 489) has been extended to include substances which contain a hydroxyl group. Not infrequently such substances are associated in the liquid state. The dissociation produced by rise of temperature is manifested by an abnormally large rate of decrease of the molecular surface energy, so that the value of k increases with rise of temperature, and does not remain constant (or decrease slightly), as is the case with unassociated liquids. If, therefore, the optically active modifications of a liquid are associated and the inactive form is an equal molecular mixture of the active forms, the expectation is legitimate that the k values of all the modifications will increase at the same rate with rise of temperature, whereas if the inactive form is a racemic compound (associated or not), material differences will be observed in the k values of the inactive and the active liquids. Unfortunately, all the liquids, the active forms of which are at present at the author's command, have proved to be unassociated between 0° and 90°, so that the preceding method of proof is unavailable. However, the practically constant and not materially different k values of the active and the inactive modifications of each of the substances examined prove, as in the case of the pinenes and the limonenes (*loc. cit.*), that the inactive modifications are not liquid racemates.

The following values of k (mean of four values between 10° and 80°) have been calculated:—Methyl-β-phenylethylcarbinol, *dl*-form 2·185, *d*-form 2·015, *l*-form 2·15; methylhexylcarbinol, *dl* form 2·045, *d*-form 1·975, *l*-form 1·91; phenylethylcarbinol, *dl*-form 2·02, *l*-form 1·96; methyl β-hydroxy-β-phenylpropionate, *dl*-form 2·33, *d*-form 2·395.

Discussion.

Dr. Dunstan pointed out that Mr. Thole had already shown that the inactive carbinols prepared by Dr. Pickard were *dl*-mixtures and not racemic compounds. He further stated that, even when racemic compounds had been found to exist in solution, the quantity present in equilibrium with the active components was always very small.

*26. "*The Water Gas Equilibrium in Hydrocarbon Flames.*" By George William Andrew.

The author has examined the equilibrium conditions as regards the reversible system $CO + OH_2 \rightleftharpoons CO_2 + H_2$ in hydrocarbon flames by exploding at varying initial pressures homogeneous mixtures of such hydrocarbons as methane, ethane, and ethylene with quantities of oxygen insufficient for complete combustion, but sufficient to prevent any deposition of carbon on explosion (for example, $CH_4 + O_2$, $2CH_4 + 3O_2$, $2C_2H_6 + 3O_2$, $2C_2H_6 + 5O_2$, $C_2H_4 + 2O_2$, &c.).

The results prove that, notwithstanding the very different maximum flame temperatures in the various experiments, the equilibrium ratios $\frac{CO \times OH_2}{CO_2 \times H_2}$ in the cooled products were nearly constant throughout the series, and practically identical with the value found by H. B. Dixon in his well known experiments on the division of oxygen between CO and H_2 in flames, thus:—

Mixture.	Mean "K" = $\frac{CO \times OH_2}{CO_2 \times H_2}$
$CH_4 + O_2$	3·98
$2CH_4 + 3O_2$	3·98
$2C_2H_6 + 3O_2$	4·12
$2C_2H_6 + 5O_2$	3·63
$2C_2H_4 + 3O_2$	3·43
Mean	3·83

It would thus appear that the experimentally determined equilibrium constant "K" does not correspond with the maximum flame temperature, but with some lower temperature in the "cooling curve" when the gases cease to react rapidly. This temperature is identified as lying somewhere between 1500° and 1600°. It was further shown that so rapidly does the equilibrium in the system $CO + OH_2 \rightleftharpoons CO_2 + H_2$ adjust itself to the falling temperature, during the cooling period down to the said temperature, that even the deposition of carbon or the recurrence of considerable quantities of methane in the products has little or no influence on the said equilibrium.

27. "*The Absorption Spectra of the Vapours and Solutions of Various Substances containing Two Benzene Nuclei.*" By John Edward Purvis.

The observations prove that all the various vapour bands of benzene are obliterated in such compounds as diphenyl, diphenylmethane, diphenylamine, diphenyl ether, &c., and all the various vapour bands of aniline in such compounds as azobenzene, azoxybenzene, benzidine, &c. In every instance the vapour bands and the solution bands are similar.

28. "*The Oxidation of some Benzyl Compounds of Sulphur. Part II. Benzyl Tetrasulphoxide.*" By John Armstrong Smythe.

When benzyl tetrasulphide is oxidised with hydrogen peroxide, benzyl tetrasulphoxide is formed in quantitative yield. Benzyl trisulphide, on oxidation, gives the same compound, in addition to benzaldehyde, sulphuric acid, and benzylsulphonic acid.

Benzyl tetrasulphoxide is a somewhat unstable compound, melting at 134—139°, and decomposing at its melting-point into benzyl disulphide and sulphur dioxide. When heated in solution, or treated with a variety of reagents, it decomposes into benzyl disulphoxide, sulphur, and sulphur dioxide, and the subsequent reaction of these products gives the clue to a number of changes which the compound undergoes.

Excess of hydrogen peroxide oxidises the tetrasulphoxide to sulphuric and benzylsulphonic acids; some benzaldehyde is also formed, as is the case with all the polysulphidic compounds of benzyl on oxidation.

Other reactions, which serve to bring out the relationship of the tetrasulphoxide with other sulphur compounds, were described.

29. "*The Reaction between Iodine and Aliphatic Aldehydes.*" By Harry Medforth Dawson and Joseph Marshall.

According to Chautard (*Ann. Chim. Phys.*, 1889, [6], xvi., 145), iodine reacts with the aliphatic aldehydes in alcoholic solution in the presence of iodic acid, and monoiodo-substitution products are formed. In some cases the substances obtained are supposed to be α-derivatives, whilst in others it is claimed that β-substitution products are produced. In view of the fact that evidence has been

obtained that halogen substitution in the aldehydes is preceded by isomeric change, and that β-substitution products cannot be accounted for, if this is the mechanism of the reaction, it was considered advisable to repeat some of Chautard's experiments.

The authors find that there is no evidence of the formation of β-iodopropaldehyde, the properties of the substance obtained being in entire agreement with the supposition that it is the α-iodo-derivative.

The statement that alkyl esters are formed when the iodoaldehydes are acted on by silver acetate is also not confirmed by the author's observations. In the case of iodoacetaldehyde, no trace of ethyl acetate was found, and the product appears to be acetylglycollaldehyde.

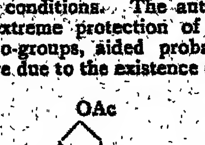
30. "*The Erosion of Lead.*" By JOHN FRANCIS LIVERSEEGE and ARTHUR WILLIAM KNAPP.

The authors have examined the action of a slightly alkaline natural water on strips of sheet lead under the conditions of the test proposed by Houston (area of 6·45 sq. cm. of lead exposed to 10 cc. of water in a test-tube), save that a duration of one day was preferred to the seven or fourteen days suggested by Houston. It was found that erosion was due to the action of oxygen in the presence of water. Carbon dioxide in an amount up to 1 per cent by volume produced little effect on the amount of erosion; when 2 or more per cent of carbon dioxide was present, erosion no longer occurred, for the liquid remained clear, and lead was dissolved (in amount less than that removed by erosion). The amount and kind of erosion was chiefly dependent on the alkalinity of the water. With alkalinity expressed as parts of calcium carbonate per 100,000 of water, (*a*) lime giving 3 to 9 parts of alkalinity reduced the erosion, but larger and smaller quantities slightly increased it; (*b*) calcium carbonate giving 4 parts of alkalinity greatly reduced erosion; (*c*) calcium carbonate giving only 2 parts of alkalinity practically prevented it. Variations in the amount of organic matter did not influence the erosion. Exposure to glass lowered the erosive quality of the water, but filtration through sand did not.

The amount of lead eroded was less the greater the distance from the lead to the water surface, and was generally proportional to the area of the surface of the lead exposed, and independent of the volume of the water.

31. "*Acylation as Influenced by Steric Hindrance: the Action of Acid Anhydrides on 3 : 5-Dinitro-p-aminophenol.*" By RAPHAEL MELDOLA and WILLIAM FRANCIS HOLLELY.

The known N-acetyl derivative of the above dinitroaminophenol is best prepared by starting from the diacetyl derivative and hydrolysing the latter by cold dilute sodium hydroxide solution. The authors find that this dinitro-*p*-aminophenol has the remarkable property of becoming acylated at the hydroxyl group with extreme facility, the O-acetyl derivative being formed by simply boiling the dinitro-compound with a little acetic anhydride diluted with acetic acid for half-an-hour or less. In these circumstances the amino-group is unattacked, and the isomeric N-acetyl and O-acetyl derivatives can accordingly be prepared by regulating the conditions. The authors attribute this property to the extreme protection of the amino-group by the ortho-nitro-groups, aided probably by an ortho-quinonoid structure due to the existence of an "inner salt" structure:—



Reasons were given, based chiefly on the marked difference in colour between the isomerides and the character of their absorption spectra (photographed by Dr. J. T. Hewitt), for assigning the above formula to the O-acetyl derivative. The authors conclude that all the nitro-derivatives of the aminophenols in which there is a nitro-group adjacent to an amino-group are best represented as "inner salts" of the above type.

32. "*The Constitution of Carbamide. Part I. The Preparation of isoCarbamides by the Action of Methyl Sulphate on Carbamides.*" By EMIL ALPHONSE WERNER.

It was pointed out that hitherto carbamide has not been known to yield by any direct reaction derivatives of the type $HN:C(OR)\cdot NH_2$, in contrast to thiocarbamide, which readily affords the sulphur analogues $HN:C(SR)\cdot NH_2$ by the direct reaction with the alkyl haloids. So far, *iso*carbamides of the types $HN:C(OR)\cdot NH_2$, $RN:C(OR)NH_2$, and $RN:C(OR)\cdot NHR$ have been obtained by the union of cyanamides and alcohols in the presence of hydrogen chloride or sodium ethoxide (Stieglitz and McKee (*Ber.*, 1900, xxxiii., 1518; and Bruce, *Journ. Am. Chem. Soc.*, 1904, xxvi., 419, 449).

It was shown that methyl*iso*carbamide and its substituted derivatives may be readily prepared from carbamide and substituted carbamides by the aid of methyl sulphate; the change takes place quantitatively in accordance with the equation—

$$HN:C{<}^{NH_2}_{OH}+(CH_3)_2SO_4=HN:C{<}^{NH_2,CH_3\cdot HSO_4}_{O\cdot CH_3}.$$

Whilst in the case of carbamide the reaction is liable to become very violent unless the temperature is carefully controlled, the change proceeds quite smoothly with the substituted derivatives. The free bases may be isolated by treating the product with sodium hydroxide solution and extracting with ether or alcohol.

The decomposition of methyl*iso*carbamide methyl hydrogen sulphate, and the substituted derivatives has been examined, and the results have furnished interesting confirmatory evidence in support of the author's views regarding the constitution of carbamide and substituted carbamides; thus, whilst the methyl*iso*carbamide salt and the derivatives of the types $HN:C{<}^{NR_2}_{O\cdot CH_3}$ and $HN:C{<}^{N:R''}_{O\cdot CH_3}$ afforded cyanuric acid and mono-N-methylcyanuric acid as part of the decomposition products, neither of these acids was obtained from the derivatives of the type $RN:C{<}^{NH_2}_{O\cdot CH_3}$ prepared from the mono-substituted carbamides.

The interaction of carbamide and methyl sulphate carried on slowly to the stage of the decomposition of the *iso*carbamide salt may be used as a quick and simple method for the preparation of pure methylamine. If the reaction is allowed to become very violent some dimethylamine is formed.

33. "*A New Formula for the Latent Heat of Vapours.*" By MALCOLM PERCIVAL APPLEBEY and DAVID LEONARD CHAPMAN.

A new formula for the heat of vaporisation of liquids, of which a preliminary account has already been published (*Proc.*, 1913, xxix., 24) was deduced from the thermodynamic principles and van der Waals' equation. The latent heats of the vapour of some common non-associated and associated compounds were calculated with the aid of the formula, and the values obtained were compared with those experimetally determined by S. Young (*Sci. Proc. Roy. Dubl. Soc.*, 1910, xii., 414).

34. "*The Electro-deposition of Zinc at High Current Densities.*" By JOHN NORMAN PRING and URLYN CLIFTON TAINTON.

At certain very high-current densities the electro-deposition of zinc can be effected in presence of a high concentration of free acid. Under these conditions the ratio of zinc to hydrogen liberated actually increases with the acid concentration up to a certain value, and also increases with the current density. In this way, with a concentration of sulphuric acid of about 15 grms. per 100 cc. and a

current density of between 20 and 50 ampères per sq. dcm. the metal can be deposited with an efficiency of about 95 per cent.

With lead anodes this electrolysis is achieved with a potential difference about 5 volts and with zinc anodes 3 volts.

The presence of small quantities of colloidal matter exerts a marked effect on this reaction, and enables the production of bright adherent deposits. The presence of the colloid also enables the application of a higher current density, and in this way raises the current efficiency.

In these solutions a very strong retardation was observed in the deposition of iron present in the electrolyte. On account of this, considerable quantities of this metal in the electrolyte caused very little contamination of the zinc.

The results obtained could not be entirely ascribed to effects of over-voltage, or surface tension, or viscosity of the electrolyte, and are probably mainly determined by influences which control the rate of the reactions involved in the change from the ionised to the free element.

The results obtained in this work indicate the most favourable conditions under which zinc can be obtained from commercial solutions, either with a view to the recovery of the metal or to its application for the purpose of electroplating.

35. "*The Ageing of Alloys of Silver and Tin.*" By William Arthur Knight.

The author has investigated the ageing of filings of alloys of silver and tin, and the densities of unaged and aged filings of the alloy Ag_3Sn. The ageing of filings of the alloy Ag_3Sn is not accompanied by a detectable change of weight, and this applies whether the ageing is carried out in coal-gas or in air. Ozone and hydrogen peroxide did not oxidise these filings at room temperature, and, further, after treatment with these oxidising agents, the filings were still unaged. From these experiments, in conjunction with others previously published, the hypothesis that the ageing of these filings is due to superficial oxidation was shown to be untenable. It was found that hydrogen sulphide at room temperature had no effect on the state of ageing of the filings. The phenomenon of ageing becomes less pronounced when the content of silver in the alloy exceeds 75 atoms per cent, solid solutions of silver in the compound Ag_3Sn thus having the same effect as the free tin in those alloys which contain less than 75 atoms per cent of silver. Density determinations showed that the density of aged filings of the alloy Ag_3Sn is greater than that of unaged filings; thus, as there is no increase in weight, there must be a contraction in volume on ageing. Dilatometer measurements confirmed this contraction, although the results did not agree accurately with those deduced from density determinations.

36. "*The Action of Phosphorus Pentachloride on the Esters of Glyceric Acid: Optically Active αβ-Dichloropropionates.*" By Percy Faraday Frankland and Andrew Turnbull.

From lævorotatory methyl, ethyl, *iso*butyl, and heptyl glycerate respectively the authors have obtained the corresponding αβ-dichloropropionates, of which the methyl compound was dextro- and the others lævorotatory. The dextrorotation of methyl αβ-dichloropropionate increases with rise of temperature, whilst the lævorotation of the others diminishes in the same circumstances. There would appear, therefore, to be no doubt that all of these dichloropropionates have the same configuration.

A more highly chlorinated inactive compound was in each case also obtained, having the molecular formula $C_3H_2Cl_5OR$, of which the probable constitution is $CH_2Cl{\cdot}CCl_2{\cdot}CCl_2{\cdot}OR$ or $CHCl_2{\cdot}CHCl{\cdot}CCl_2{\cdot}OR$, in which R stands for methyl, ethyl, *iso*butyl, and heptyl respectively (see also *Trans.*, 1913, ciii., 718).

(To be continued).

PHYSICAL SOCIETY.

Annual General Meeting, February 13, 1914.

Prof. C. H. Lees, F.R.S., Vice-President, in the Chair.

The Report of the Council was taken as read.

Mr. T. Smith asked leave to draw attention to certain disadvantages of the present method of electing the Council. For reasons which he gave he thought there ought to be a change in the method of ballot. He suggested that the Council should issue its list earlier than at present, and allow Fellows to send in other nominations if they so desired. The final balloting list should contain the names of everyone nominated. He thought that this would lessen the risk of inadequate representation of any important branch of physics upon the Council and of more than adequate representation of others. He saw no reason why the statutes should not be altered if necessary to make this possible.

The Chairman said he had no doubt that the Council would carefully consider Mr. Smith's suggestions.

Mr. E. F. Etchells thought it would be advisable on the present occasion, before the committee on scientific nomenclature had got to work, to emphasise the importance of adopting the system already accepted by engineers. He outlined some of the principles, and hoped that the committee would make itself familiar with the existing schemes before reaching any decision.

Dr. Eccles assured the speaker that this was being done.

The Treasurer's Report was then read by Mr. Duddell.

The reports of the Council and Treasurer were adopted.

Votes of thanks to the Auditors, the Officers and Council, and the Governing Body of the Imperial College were carried unanimously, the respective proposers and seconders being Dr. G. W. C. Kaye and Mr. E. F. Etchells, Mr. C. W. S. Crawley and Mr. A. Campbell, and Prof. J. W. Nicholson and Major O'Meara.

The following is the list of officers elected for the ensuing year:—

President—Sir J. J. Thomson, O.M., D.Sc., F.R.S.

Vice-Presidents (who have filled the office of President)—Prof. G. C. Foster, F.R.S., Prof. W. G. Adams, M.A., F.R.S., Prof. R. B. Clifton, M.A., F.R.S., Prof. A. W. Reinold, C.B., M.A., F.R.S., Prof. Sir Arthur W. Rücker, M.A., D.Sc., F.R.S., Sir W. de W. Abney, R.E., K.C.B, D.C.L., F.R.S., Prin. Sir Oliver J. Lodge, D.Sc., F.R.S., Prof. S. P. Thompson, D.Sc., F.R.S., R. T. Glazebrook, D.Sc., F.R.S., Prof. J. H. Poynting, M.A., F.R.S., Prof. J. Perry, D.Sc., F.R.S., C. Chree, Sc.D., F.R.S., Prof. H. L. Callendar, M.A., F.R.S., Prof. A. Schuster, Ph.D., F.R.S.

Vice Presidents—Prof. T. Mather, F.R.S., A. Russell, M.A., D.Sc., F. E. Smith, R. S. Whipple.

Secretaries—W. R. Cooper, M.A., 82, Victoria Street, S.W., S. W. J. Smith, M.A., D.Sc., Imperial College of Science and Technology, S. Kensington.

Foreign Secretary—R. T. Glazebrook, D.Sc., F.R.S.

Treasurer—W. Duddell, F.R.S., 56, Victoria Street, S.W.

Librarian—S. W. J. Smith, M.A., D.Sc., Imperial College of Science and Technology.

Other Members of Council—W. H. Eccles, D.Sc., Sir R. A. Hadfield, F.R.S., Prof. G. W. O. Howe, M.Sc., Prof. J. W. Nicholson, M.A., D.Sc., Major W. A. J. O'Meara, C.M.G., C. C. Paterson, Prof. O. W. Richardson, M.A., D.Sc., F.R.S., Prof. the Hon. R. J. Strutt, F.R.S., W. E. Sumpner, D.Sc., R. S. Willows, M.A., D.Sc.

Assist. Secretary and Reporter—J. Guild, A.R.C.S., D.I.C.

A Paper entitled "*On the Moving Coil Ballistic Galvanometer.*" By R. Ll. Jones, M.A., was read by Mr. A. Campbell.

The author first considers the mathematical theory of a moving coil galvanometer in which the damping is such as to make the motion non-oscillatory; then an account is given of some observations on a galvanometer which confirm some of the deductions from the theory, and the results obtained are applied to find the relation between the galvanometer throw and the change of flux in the search coil which produces it.

Discussion.

Prof. C. H. Lees thought it likely that with a highly damped galvanometer the creeping at the end would create a difficulty as to what reading to take.

Prof. T. Mather stated that the creep presented no difficulty, since it was easy to get the maximum deflection reached. The real difficulty was in getting the true zero.

Mr. A. Campbell mentioned that although the case of the strongly damped galvanometer when used with a search coil did not appear to be treated in any English text-book, he had found it described in Kohlrausch's "Lehrbuch der praktischen Physik" (10th edition, 1905).

A Paper "*On Vibration Galvanometers of Low Effective Resistance*" was read by Mr. A. Campbell.

The mathematical theory of the motion of the moving coil of a vibration galvanometer is first given (partly following Wenner), and simple relations are shown to hold between the two resonance frequencies, the free frequency and the amplitude time constant. It is also shown how all the constants of the equation of motion can be deduced from observations of the direct and alternating-current sensitivities, the alternating voltage sensitivity, and the "dead" resistance. A complete table of the observed and deduced constants is given for a series of very small coils, the number of turns in these varying from 1 to 40. The current sensitivities range from 6 mm. to 160 mm. at 1 m. per microampere at 100 vibrations per second, the corresponding effective resistances being about 9 and 1500 ohms respectively. It is pointed out that the selectiveness (for given current) due to resonance is mainly determined by the absolute value of the "amplitude time constant"; the more sluggish a galvanometer is in settling to zero the more selective will it be.

Discussion.

Dr. Russell thought everyone was indebted to Mr. Campbell for popularising the resonance galvanometer. In the present Paper the use of the amplitude time constant struck him as being very neat.

Prof. G. W. O. Howe pointed out that one method of determining the no-load losses of a motor was to cut off the supply and observe the rate of slowing down. From this the losses could be calculated and the efficiency found. This, in effect, was what Mr. Campbell did with the vibration galvanometer, and there seemed to be many analogous points in the two processes.

Mr. Campbell thought Prof. Howe's analogy was extremely good. He added that a coil tested at 50 vibrations per second gave a current sensitivity of 500 mm. at 1 metre per microampere with an effective resistance of 2500 ohms.

A Paper "*On Vacuum-tight Lead Seals for Leading-in Wires in Vitreous Silica and other Glasses,*" was read by Dr. H. J. S. Sand.

The author has found out that lead which has been allowed to solidify in contact with glass will, if free from oxide, form a vacuum-tight joint with the latter. Owing to the very great firmness with which the metal adheres, and owing to its great plasticity, these joints can stand temperature changes without damage. When applied to quartz, the joints are usually made inside a tube in conjunction with a molybdenum wire seal as follows:—The tube is shaped so that the molybdenum wire can be placed loosely inside it. A short piece of the latter is later sealed into the quartz, whereas one of its ends projects a few millimetres into the space in which the lead seal is to be made. Connected with this space by a short capillary there is an upper chamber in which the piece of lead is placed. The air is first blown out with hydrogen, and the tube then closed at the top and evacuated to a pressure of a millimetre or two. The quartz is then softened and pinched on to the molybdenum wire. After this the lead is melted and allowed to filter from oxide through the capillary and run into the space shaped to receive it, which has been highly heated. Before it has solidified, the tube is broken at the top to allow the pressure of the atmosphere to force the lead well against the surface of the glass. The tube is then cut at a suitable place and a tinned leading-in wire introduced into the lead. Such seals have been successfully fitted to vacuum tubes, mercury lamps, &c., and when made as described have so far not been known to fail.

Discussion.

Prof. C. H. Lees asked how the cost of the process compared with that of the ordinary platinum seals in the case of glass.

Dr. Sands, in reply, stated that platinum seals could be made with such small quantities of platinum that it was hopeless to try to compete with them in point of cheapness.

NOTICES OF BOOKS.

The Sampling and Assay of the Precious Metals. By Ernest A. Smith, Assoc.R.S.M. London: Charles Griffin and Co., Ltd. 1913.

This treatise on the sampling and assay of the precious metals is intended for the use of both practical assayers and students, the requirements of the latter class of readers having been specially considered. It will be found admirable for both purposes, being thoroughly practical and comprehensive, and the descriptions of methods of sampling, and of the principles of the valuation and sale of ore and bullion, will be particularly valuable to assayers. "The precious metals" include gold, silver, platinum, and the platinum metals, and methods of determining them are described in considerable detail. The first eleven chapters deal with the general principles of assaying, the design and equipment of offices, the choice and use of apparatus, and the sampling of specimens, which latter subject is considered in much greater detail than is usual in books on metallurgy and assaying. The later chapters are devoted to the assay of gold and silver bullion, base bullion, alloys, and ores, and an adequate account is also given of the laboratory work of a cyanide mill.

A Practical Manual of Autogenous Welding (Oxyacetylene). By R. Granjon and P. Rosemberg. Translated by D. Richardson, Wh.Ex., A.M.I.M.E. London: Charles Griffin and Co., Ltd. 1913.

The process of autogenous welding by the oxyacetylene blowpipe was discovered not much more than twelve years ago, but it is already employed in thousands of workshops, and engineers and manufacturers have quickly realised its great value. The knowledge, however, of the principles involved is distinctly behind that of the practice, in this country at any rate, and hitherto no book in the English language has been obtainable which dealt with the theory and technology of the process. Hence there is no doubt but that this book will be warmly received. The original French work reached its second edition within a year of publication, and the translation has been made from the revised edition, which embodies all the latest advances. It is written mainly for the practical man, and full information is given relating to the materials, methods, and manipulation. Prices, weights, &c., are given in English as well as in French units, and the translator has added some notes relating to English regulations and practice,

Handbook on Petroleum. By Captain J. H. Thomson and Sir Boverton Redwood. Third Edition. Revised and Added to by Major A. Cooper Key and Sir Boverton Redwood, Bart. London: Charles Griffin and Co., Ltd. 1913.

In the new edition of this widely used handbook for inspectors under the Petroleum Acts the chapter on sources of supply has been partly re written, and the accounts of the storage and distribution of petroleum products has been extended. It has not been found necessary to make many alterations in the chapters dealing with legislation, but the appendices have been brought down to date by the inclusion of the most recent orders.

Elementary Practical Chemistry. Part I. *General Chemistry.* By Frank Clowes, D.Sc. (Lond.), and J. Bernard Coleman, A.R.C.Sc. Sixth Edition. London: J. and A. Churchill. 1914.

In the sixth edition of this valuable book a new section has been added on phosphorus and some of its simpler compounds, silica, and the silicates and glass. It also contains two new sections on some of the common metals, in which the properties of and tests for the metals are given, and experiments involving the preparation and reactions of their salts are described. The text has also been revised throughout, but only very few and unimportant corrections have been found necessary.

The International Whitaker. London: J. Whitaker and Sons, Ltd. New York: The International News Co. 1914.

This handbook contains accounts of the government, finance, products, industries, commerce, &c., of all the countries of the world. It is issued at a very moderate price, and will be found invaluable for schools and colleges as a reference book, to correct or supplement the data given in geographical text-books. The information contained in it has been revised in every instance from official sources, and in many cases by Government Departments.

Carnotite, the Principal Source of Radium. By Thomas F. V. Curran. 1913.

This pamphlet has been issued by Messrs. Curran and Hudson, dealers in radium products, radio-active ores, &c., and contains short accounts of the chemical nature and occurrence of carnotite. The cost of mining the ore is discussed, and its metallurgy and the extraction of radium are also described. The pamphlet contains in addition a brief account of the uses of radium, and abstracts of the report of the British Radium Institute, issued in 1913, and of the government publications of Austria-Hungary as to its employment in therapeutics.

The Manuring of Market Garden Crops. By Bernard Dyer, D.Sc., F.I.C., and F. W. E. Shrivell, F.L.S. New Edition. London: Vinton and Co., Ltd. 1913.

This book contains a detailed account of the authors' experimental work in market gardening at Hadlow, Tonbridge, which was begun in 1894. The main object of the work was to discover how far the large quantities of stable manure purchased by market gardeners are necessary, and in what circumstances artificial fertilisers can be substituted for them. A large variety of vegetable and fruit crops was investigated; in fact, practically all those commonly grown in England, and the results in the case of each individual crop are tabulated, illustrated, and discussed. Very precise practical recommendations are given, based upon the authors' experiments, and questions of cost are carefully considered. The book should be in the hands of all market gardeners, and the authors' advice on the use of artificial fertilisers will be of the greatest value, especially in view of the fact that it seems probable that stable manure will be an almost unobtainable article of commerce in the near future.

Ozonair Apparatus for Therapeutical Applications.

This pamphlet, issued by the Ozonair Company, Ltd., gives short non-technical descriptions of the forms of portable apparatus made for the production of ozone for inhaling, and disinfecting and deodorising purposes. Some details are included regarding the initial and running costs, the latter being described as almost negligible, and other pamphlets relating to other applications of the apparatus can be obtained from the offices of the company, 96, Victoria Street, Westminster.

Aichiken Commercial Museum, Nagoya, Japan.

This pamphlet contains some account of the aims and equipment of the Aichiken Commercial Museum, which the authorities of the city of Nagoya are strenuously trying to bring to the highest pitch of efficiency and usefulness. Nagoya has been called the Birmingham of Japan, and the museum is destined to be one of the largest and best equipped in the country. The account is written in what may be described as "credible" English, to borrow an expression from the text, and the illustrations are excellent. To celebrate the third anniversary of the opening of the museum an exhibition of samples, circulars, and catalogues is to be held from March 1 to April 30 of the current year. Foreign manufacturers are invited to forward exhibits, and further particulars may be obtained from the Museum.

CORRESPONDENCE.

SOME ANOMALOUS VARNISH VISCOSITIES.

To the Editor of the Chemical News.

Sir,—I shall be glad if some of your readers can explain the cause of some anomalous results obtained by me in the determination of viscosity of oil varnishes by means of a Doolittle's torsion viscometer. The varnish referred to here was a very thick black stoving varnish, and it was sought to determine the effect of increase of temperature upon its viscosity. The viscometer used is an application of the torsion pendulum, and is described in the *Journ. Am. Chem. Soc.*, 1883, clxxiii., 454, and in Allen's "Commercial Organic Analysis," vol. ii., part 2, p. 125. The "bob," which is immersed in the liquid, is a brass cylinder $2'' \times 1\frac{1}{4}''$, which is attached to a heavier brass weight with disc graduated in degrees (above it and out of the liquid), and the whole is suspended by a tempered steel wire of 0·295 mm. diameter (0·0116 inch) and 21 inches long.

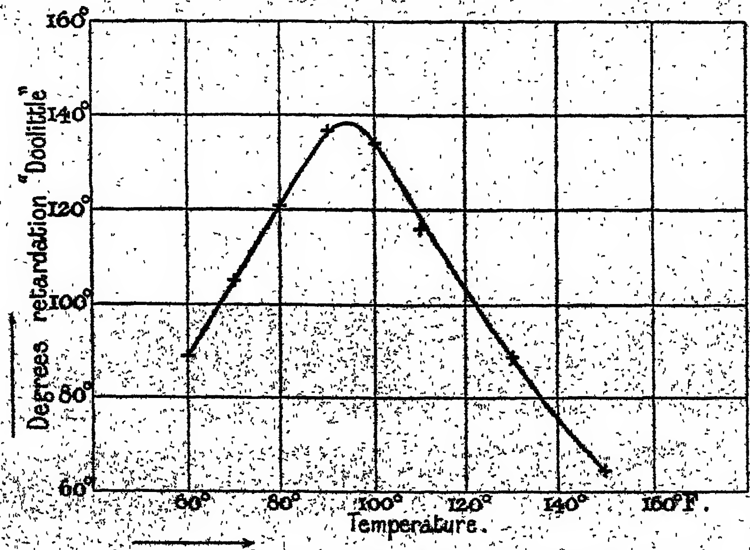
The "bob" being immersed in the liquid, the wire is rotated 360° and the cylinder allowed to swing free. The instrument measures the amount of damping between the first and second swings in the same direction, and this damping is read in angular degrees. Two tests are made in opposite directions to minimise any error which might be due to the instrument not having been adjusted to zero.

The effect of increase of temperature on a varnish is to cause it to become thinner, but it is here where the anomaly comes in. I give the figures obtained:—

Temperature (°F.)	60	70	80	90	100	110	130	150
Degrees retardation	89	105	121	137	134	116	89	65

These results have been plotted in the accompanying graph.

It will be seen that an increase of temperature from 60° to 90° F. has increased the apparent viscosity, but from 100° to 150° F. the viscosity decreases in a normal manner. These results are not due to errors of experiment, because similar results have been obtained from other oil varnishes. Even gradual additions of oil of turpentine to a thick



Influence of Temperature upon Viscosity of a Black Stoving Varnish.

varnish has given similar increase to a maximum, and then a decrease. The viscosities, as a matter of fact, *do not increase* with rise of temperature, but the curious results here given are due to some physical property, which I should be glad to have explained.—I am, &c.,

THOMAS A. DAVIDSON.

"Ardlui," 37, Strathyre Avenue, Norbury, S.W., February 2, 1914.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Bulletin de la Société Chimique de France.
Vol. xv.-xvi., No. 1, 1914.

Thermic and Cryoscopic Studies of Mixtures of Benzene and Ethyl Alcohol.—F. Viala.—The specific heat of a mixture of ethyl alcohol and benzene is appreciably greater than the value obtained by calculation; there is a relation between the specific heat of the mixture and its heat, and the former seems to be a function of the concentration. The molecular association of ethyl alcohol in solution in benzene increases with the concentration. In dilute solution all the molecules are simple. The molecular weight is given by $C_2H_6O = 46$. In concentrated solution all the molecules are double, and the molecular weight is 92.

Double and Complex Cyanates.—Paul Pascal.—The author has demonstrated the existence of four cyanates derived from uranium:—1. The greenish yellow complex salt, $[UO_2(CNO)_4]K_2$. 2. Its normal product of hydrolysis, $(UO_2)_2(CNO)_5K$. 3 and 4. The decomposition products, uranyl cyanate, $UO_2(CNO)_2$, and the double cyanate, $UO_2(CNO)_3K$, both golden-yellow in colour. Solutions which are rich in alkaline cyanate contain the potassium salt of a divalent acid, easily dissociated by water:—$[UO_2(CNO)_4]K_2$. The dissociation of cobalto cyanates is even greater than that of uranyl cyanate, but becomes about the same when excess of alkaline cyanate is added, which suggests that the two complexes have identical constitutions.

Action of Dimethylamine upon the Two Chloro-oxyisobutyric Acids and their Derivatives.—E. Fourneau and M. Tiffeneau.—By heating with organic potassium salts the chloro oxyisobutyric ethers are readily transformed into mixed ether salts in which, by the action of thionyl chloride, the hydroxyl can be replaced by an atom of chlorine. By saponification with dilute hydrochloric acid the isomeric chloro-oxyisobutyric acid is obtained. The action of dimethylamine upon these two isomeric acids and their ethers gives the same product. Thus:—

$$\begin{array}{l} \text{I. } CH_2OH.CClCH_3CO_2R \\ \text{II. } CH_2Cl.COH.CH_3CO_2R \end{array} \rightarrow \begin{array}{l} CH_3 \\ CH_3 \end{array}\!\!> NCH_2\underset{|}{C}OHCH_3. \atop \qquad\qquad\qquad CO_2R$$

Hence, obviously in I. the atom of hydrogen is not simply replaced by the amine, but the intermediate formation of oxide of ethylene occurs.

Stereo-isomeric Camphane Carbonic Acids.—Ph. Barbier and V. Grignard.—To prepare solid or B pinene hydrochloride, dry hydrochloric acid is saturated with an alcoholic solution of pinene at 75—80°. The liquid hydrochloride distils at 80—82° under 13 mm. Between 84° and 90° under 13 mm. a portion distils which yields a solid hydrochloride. When the hydrochlorides B and A are converted into magnesium derivatives and oxidised, they both yield mixtures of borneol and isoborneol, lævorotatory in both cases, but decidedly more active in the second case than in the first. If the hydrochlorides are converted into acids B gives a dextrorotatory acid fusible at 76—78°. This acid readily isomerises to give a lævo acid fusing at 88—89°. With A a lævo acid fusing at 73—74° is obtained, and as before it isomerises to give a lævo acid of melting-point 86—87°. In spite of the difference of melting-point these two acids are identical. Heating with aromatic amines transforms the acids into their stable isomer. There is complete parallelism between the isomerisation of the camphane carbonic acids and that of the camphols, and like the camphols the α and β acids possess the property of crystallising together in many proportions.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xlvi., No. 17, 1913.

Influence of Foreign Substances upon the Activity of Catalysts.—C. Paal and M. Windisch.—Of the metals only magnesium and nickel do not influence the power of

platinum of rendering hydrogen active. Aluminium, cobalt, and bismuth very greatly weaken this power, while iron, copper, zinc, silver, tin, and lead remove it altogether. The oxide and carbonate of magnesium also have no effect; lead carbonate behaves like the metal, and the basic nitrate of bismuth makes the platinum almost completely passive.

Active Nitrogen.—Erich Tiede and Emil Domcke.—Strutt stated that the yellow luminescence produced when an electrical discharge occurs in nitrogen is due to the formation of a chemically active modification, and this view was confirmed by Koenig and Elöd. It was supposed that the appearance of the luminescence was due to the conversion of active into ordinary nitrogen. The authors, however, have found that it is not obtained with pure nitrogen, but is dependent upon the presence of oxygen. It is, in fact, a very sensitive test for oxygen in nitrogen.

Atti della Reale Accademia dei Lincei.
Vol. xxii. [ii.], No. 10, 1913.

Palladous Nitrites of Divalent Metals Fixed by means of Organic Bases.—G. Scagliarini and G. B. Rossi.—The extreme solubility of the palladous nitrites of divalent metals makes it impossible to obtain them in the solid state, but hexamethylene tetramine is a convenient reagent for fixing them. By its action compounds of the formula $MePd(NO_2)_4.8H_2O+2C_6H_{12}N_4$, where Me = Mg, Mn, Ni, or Co, have been obtained. Of these the compounds of magnesium and manganese are yellow, while those of nickel and cobalt are respectively emerald green and brick-red. The derivatives are isomorphous with one another, and give mixed crystals in all proportions.

MISCELLANEOUS.

Institution of Petroleum Technologists.—Inaugural Meeting, Tuesday, March 3, 8 p.m., at the Royal Society of Arts, John Street, Adelphi. Sir Boverton Redwood, Bart., presiding.

Institute of Metals.—The Annual General Meeting of the Institute of Metals will be held at the Institution of Mechanical Engineers, Storey's Gate, Westminster, S.W., on Tuesday and Wednesday, March 17 and 18, 1914. The meeting will commence at 3 p.m. on March 17, and 10.30 a.m. on March 18.

Programme.—Tuesday, March 17: General Meeting of Members in the Hall of the Institution of Mechanical Engineers. Report of the Council on the work of the past year will be presented by the President. The Hon. Treasurer, Prof. T. Turner, M.Sc., will present his Report. The results of the ballots for the Council for 1914 and for the election of new members will be declared. The newly-elected President will deliver his Inaugural Address. The Fifth Annual Dinner of the Institute of Metals at the Criterion, Restaurant, Piccadilly Circus, W., 8 p.m. Wednesday, March 18: General Meeting of Members in the Hall of the Institution of Mechanical Engineers. A selection of Papers will be read and discussed.

Papers.—The following is a list of the Papers and Reports that are expected to be submitted on March 18:—

First Report to the Beilby Research Committee, dealing with the solidification of metals from the liquid state, by C. H. Desch, Ph.D., D.Sc.

"Bronze," by J. Dewrance.

"Vanadium in Brass: The Effect of Vanadium on the Constitution of Brass containing 50 to 60 per cent of Copper," by R. J. Dunn, M.Sc., and O. F. Hudson, M.Sc.

"The Quantitative Effect of Rapid Cooling on Binary Alloys" (second Paper), by G. H. Gulliver, B.Sc.

"Crystal Protomorphs and Amorphous Metal," by Prof. A. K. Huntington, A.R.S.M.

First Report of the Nomenclature Committee.

"The Influence of Nickel on some Copper-aluminium Alloys," by Prof. A. A. Read, M.Met., F.I.C., and R. H. Greaves, M.Sc.

"Muntz Metal: The Correlation of Composition, Structure, Heat Treatment, and Mechanical Properties, &c.," by J. E. Stead, D.Sc., D.Met., F.R.S., and H. G. A. Stedman, A.M.I.E.E.

"The Micro-chemistry of Corrosion" (Part II.), by S. Whyte, B.Sc., and C. H. Desch, Ph.D., D.Sc.

MEETINGS FOR THE WEEK.

Monday, March 2nd.—Royal Society of Arts, 8. (Cantor Lecture). "Artistic Lithography," by Joseph Pennell.

— Royal Institution, 5. General Meeting.

— Society of Chemical Industry, 8. "Bleaching of Chemical Pulp, and Suggestions for a Standard Method in Test Cases," by A. Baker and J. Jennison. "Blasting Gelatin, some Notes and Theories," by W. A. Hargreaves. "Application of Calcium Carbide to the Formation of Alloys," by W. R. Hodgkinson.

Tuesday, 3rd.—Royal Institution, 3. "Modern Ships," by Prof Sir John H. Biles, D.Sc., &c.

— Royal Society of Arts, 4.30. Discussion on the Paper by Sir Robert W. Perks, Bart., on "The Montreal, Ottawa, and Georgian Bay Canal."

— Institution of Petroleum Technologists, 8. "Geometry of the Anticline," by Sir T. H. Holland. "Educational Aims of the Institution of Petroleum Technologists," by E. H. Cunningham-Craig, "Petroleum Technology as a Profession," by Prof. V. B. Lewes.

Wednesday 4th.—Society of Public Analysts, 8. "Composition and Analysis of Compound Liquorice Powder," by A. E. Parkes and F. Major. "Composition of the Saline Matter adhering to certain Wet Salted Skins," by M. C. Lamb. "Determination of Carbon Monoxide in Air," by F. S. Sinnatt and B. J. Cramer. "Suggested Simple Method for the Approximate Determination of 'Stump' (Wood) Turpentine in American Gum Turpentine," by L. M. Nash. "Dried Caricæ Papaya Juice," by F. F. Shelley.

— Royal Society of Arts, 8. "Travels in the Balkan Peninsula," by H. C. Woods.

Thursday, 5th.—Royal Institution, 3. "Heat and Cold," by Prof. C. F. Jenkin, M.A.

— Royal Society. "Action of Light on Chlorophyll," by H. Wager. "Formaldehyde as an Oxidation Product of Chlorophyll Extracts," by C. H. Warner. "Controlling Influence of Carbon Dioxide in the Maturation, Dormancy, and Germination of Seeds," by F. Kidd. "Functional Correlation between the Ovaries, Uterus, and Mammary Glands in the Rabbit, with Observations on the Oestrous Cycle," by J. Hammond and F. H. A. Marshall. "Chromaffine System of Annelids and the Relation of this System to the Contractile Vascular System in the Leech, *Hirudo medicinalis*," by J. F. Gaskell.

— Chemical, 8.30. "Re-determination of the Atomic Weight of Vanadium," by H. V. A. Briscoe and H. F. V. Little. "Isomerism of the Oximes—Part III., The Hydroxybenzaldoximes," by C. L. Brady and F. P. Dunn. "Constituents of the Leaves and Stems of *Daviesia latifolia*," by F. B. Power and A. H. Salway. "Composition of some Mediæval Wax Seals," by J. J. Dobbie and J. J. Fox. "Experiments on the Rate of Nitrification," by R. M. Beesley. "Studies on the Constitution of Soap Solution—the Alkalinity and Degree of Hydrolysis of Soap Solutions," by J. W. McBain and H. E. Martin. "Influence of Configuration on the Condensation Reactions of Polyhydroxy Compounds—Part I., Constitution of Mannitol Triacetone" and "Formation of Ethers from Mannitol—an Example of Steric Hindrance," by J. C. Irvine and B. M. Paterson. "Relative Strengths of Ammonium and the Substituted Ammonium Hydroxides as Measured by their Action on a Pseudo Base," by C. K. Tinkler. "Interaction between Nitric Acid and Brucine in the presence of Metallic Nitrates," by E. H. Rennie and A. E. Dawkins."

Friday, 6th.—Royal Institution, 9. "The Stage Irishman," by The Rev. Canon J. O. Hannay, M.A. ("George A. Birmingham").

Saturday, 7th.—Royal Institution, 3. "Recent Discoveries in Physical Science," by Prof. Sir J. J. Thomson, O.M., F.R.S.

THE CHEMICAL NEWS.

VOL. CIX., No. 2832.

THE DISCOVERY OF SIMPLER METHODS OF OBTAINING FORMIC ACID IN QUANTITY.

By F. D. CHATTAWAY.

THE earlier methods of obtaining formic acid ceased to be of any practical importance when Gay Lussac,* in 1831, discovered that it is produced when oxalic acid is heated. He observed that oxalic acid submitted to the action of heat, in part volatilised and in part decomposed, giving a mixture of carbonic acid and an inflammable gas. To ascertain the nature of the latter he put crystallised oxalic acid into a glass retort, and exposed it to a gradually augmented heat. He found that the crystals melted at 98°, and that at 110°, together with the vapour of water, an elastic fluid was disengaged, the amount of which increased as the loss of water of crystallisation allowed the temperature to rise. At 120°–130° the disengagement of gas was extremely rapid, and continued until the acid was completely destroyed. He noted that the gas liberated was a mixture of 6 parts of carbonic acid and 5 parts of carbonic oxide, while in the similar mixture obtained by heating oxalic acid with sulphuric acid equal amounts of the same gases were found. This led him to think that some substance other than water and the oxides of carbon must be formed. On examining the liquid distillate he found it to be acid, and showed that the acidity was due to formic acid.

At first, while the water of crystallisation was being given off, formic acid was only produced in inconsiderable quantity, but more was formed as the decomposition proceeded, and towards the end of the operation when the oxalic acid had become desiccated the distillate had a very penetrating odour and pungent taste.

From the composition of the gas evolved he concluded that 12 parts of oxalic yielded 1 part of formic acid, and noted that the oxalic acid did not sensibly volatilise, but completely decomposed when not too rapidly heated.

This method was so much more simple and convenient than any oxidation method that it soon came into general use, and various improvements in procedure were devised; thus, Gerhardt,† in 1843, says:—"Oxalic acid decomposes into formic acid by heat—it is indeed the best means of preparing the latter; one knows that the employment of sugar or of starch necessitates large apparatus, and never gives a very pure product. I use oxalic acid mixed intimately with very fine sand, and submit the whole to distillation in a glass retort. The operation scarcely needs watching, and the product is very concentrated. It only has to be distilled once in order to free it from any undecomposed oxalic acid. The gas which is disengaged during the operation consists of carbonic acid and carbonic oxide, but the proportion of the latter is not constant, and it appears that it is produced by decomposition of the formic acid."

Other methods of preparing formic acid were soon forthcoming. These we owe, in the first instance, to the extraordinary chemical instinct of Berthelot. Berthelot made a notable discovery in 1855. He shook up ethylene with sulphuric acid, and having diluted the solution with water distilled it, thus synthesising alcohol. This conversion of ethylene into alcohol led Berthelot to another and more important discovery.

It had long been known that ethyl alcohol when heated with sulphuric acid yields ethylene and water, while formic acid similarly heated with sulphuric acid yields

* Ann. Chim. Phys., 1831, xlvi., 218.

† Ann. Chim. Phys., 1843, [3], vii., 129.

carbonic oxide and water. He argued that since the former process could be reversed the latter might also. This, in a sense, he succeeded in effecting* by allowing carbon monoxide to act on potash at a raised temperature. He placed 10 grms. of damp potash in a half litre flask filled with carbon monoxide, sealed it up, and heated it in a water-bath for seventy two hours. When the flask was opened under mercury the gas was found to have been completely absorbed, and on dissolving the solid product in water, acidifying with dilute sulphuric acid, and distilling, formic acid was obtained.

Berthelot did not work out the details of this process or suggest its use as a method of preparing formic acid. This was done nearly forty years later by Merz and Tirbirica.† During the last twenty years it has become the technical method of manufacturing formic acid, which has, in consequence, become so cheap that it is now extensively used.

Berthelot almost at the same time discovered a second method of making formic acid, which, until it was manufactured on a large scale from carbon monoxide, was almost exclusively used, and is still the most convenient laboratory method.‡

During the years 1853–1854 Berthelot was engaged in studying the action of acids upon glycerol, and one can hardly doubt that in the course of this investigation he heated among others oxalic acid with glycerol. It was thus chance rather than the deliberate attempt to find a method of combining carbonic acid in the nascent state with water, which he advances in his paper, that led him to the discovery that formic acid is thereby produced.

Berthelot found§ that when oxalic acid, glycerol, and a little water were heated together for from twelve to fifteen hours at 100° C. practically half the carbon of the oxalic acid escaped as carbon dioxide, and that the remaining half could be obtained as formic acid by distilling the residue with water. He regarded the glycerol simply as furthering by contact the decomposition of the oxalic acid, and considered that after the evolution of the carbon dioxide the formic acid remained dissolved in the glycerol "as ammonia in water."

Berthelot's method of obtaining the formic acid by distilling the residue repeatedly with water was inconvenient and tedious, and was soon replaced by the familiar continuous process which was worked out in great detail by Lorin, at first in Berthelot's laboratory.|| The common method of preparing allyl alcohol from glycerol is an indirect consequence of Berthelot's work, as it was discovered by Tollens when preparing formic acid by Lorin's method. He did not at first¶ properly regulate the heat, and obtained a product of extraordinarily pungent smell which violently attacked the eyes. From the distillate a liquid not miscible with water was separated which proved to be allyl formate. Subsequent work showed that allyl alcohol was produced in large quantity when oxalic acid and glycerol were rapidly heated together to the temperature at which the evolution of CO_2 again became vigorous after having markedly slackened.

It is a curious circumstance that only within the last few months has a satisfactory explanation of the course of these reactions been put forward.

That given in different text books varies somewhat, but, speaking generally, the statement is made that at about 100° C. the oxalic acid decomposes into carbon dioxide and formic acid, the latter then reacting with the glycerol to

* Comptes Rendus, 1856, xlii., 955; Ann., 1856 xcvii., 125.

† Ber., 1880, xiii., 23.

‡ Kolbe and Schmitt's synthesis (Annalen, 1861, cxix., 251) of formic acid from carbon dioxide may be referred to here. They state that the action goes very easily, and express surprise that it has not long ago been observed. Metallic potassium in thin shavings was placed on a shallow dish over water under a bell-jar, and carbonic acid was continuously led in. After twenty-four hours the metal was found to be converted into a mixture of potassium bicarbonate and potassium formate.

§ Comptes Rendus, lii., 447; Ann., 1856, xcviii., 139.

|| Bull. Soc. Chim., 1866, [2], v., 7.

¶ Zeitschrift für Chemie, 1866, ii., 518.

produce monoformin. This, on the addition of a further quantity of the crystallised acid, is hydrolysed by the water of crystallisation which is given off, the formic acid liberated distilling over while the oxalic acid left decomposes as before, yielding formic acid which in its turn reacts with the regenerated glycerol, thus:—

$$\begin{array}{l} CO.OH \\ | \\ CO.OH \end{array} \rightarrow \begin{array}{l} H \\ | \\ CO.OH \end{array} + CO_2 \xrightarrow{\text{Glycerol}} \begin{array}{l} CH_2.O.CO.H \\ | \\ CH.OH \\ | \\ CH_2.OH \end{array}$$

$$\begin{array}{l} CH_2.O.CO.H \\ | \\ CH.OH \\ | \\ CH_2.OH \end{array} \xrightarrow{H_2O} \begin{array}{l} CH_2.OH \\ | \\ CH.OH \\ | \\ CH_2.OH \end{array} + \begin{array}{l} H \\ | \\ CO.OH \end{array}$$

this cycle of operations being capable of repetition as often as desired.

The production of allyl alcohol when a mixture of oxalic acid and glycerol is rapidly heated to about 250° is invariably stated to be due to a decomposition which the monoformin produced as above undergoes, whereby it splits up into allyl alcohol, carbon dioxide, and water, thus:—

$$\begin{array}{l} CH_2.O.CO.H \\ | \\ CH.OH \\ | \\ CH_2.OH \end{array} \longrightarrow \begin{array}{l} CH_2 \\ \| \\ CH \\ | \\ CH_2.OH \end{array} + CO_2 + H_2O$$

These explanations are fundamentally incorrect. A moment's consideration suggests that the first reaction is unlikely to be a decomposition of oxalic acid into formic acid and carbon dioxide, since oxalic acid does not decompose to any appreciable extent until a temperature is reached much above anything ever recommended in the method under discussion.

That the second assumed reaction, the decomposition of the monoformin by the water of crystallisation liberated when the further amount of crystallised oxalic acid is added, is not the main source of the formic acid which distils over, is shown by the well known fact that neither water nor crystallised acid need be used, since, if anhydrous oxalic acid is added, a distillate containing over 98 per cent of formic acid can easily be obtained.

That some compound must be formed before carbon dioxide makes its appearance is clear, since, while other polyhydric alcohols may be used in place of glycerol, the temperature at which the evolution of gas begins to be rapid varies considerably, depends upon the alcohol employed, and is not within narrow limits the same, as it would be were the oxalic acid itself decomposing.

The true explanation* is the obvious one. The oxalic acid reacts with glycerol† as it does with other alcohols, both an acid and a normal oxalate being produced.

$$\begin{array}{l} CH_2.OH \\ | \\ CH.OH \\ | \\ CH_2.OH \end{array} + \begin{array}{l} CO.OH \\ | \\ CO.OH \end{array} \begin{array}{l} \nearrow \begin{array}{l} CH_2.O.CO.CO.OH \\ | \\ CH.OH \\ | \\ CH_2.OH \end{array} \\ \searrow \begin{array}{l} CH_2.O.CO \\ | \qquad\quad | \\ CH.O.CO \\ | \\ CH_2.OH \end{array} \end{array}$$

The former like all such compounds is unstable at a slightly elevated temperature, and decomposes when this is reach-d into carbon dioxide and monoformin, thus:—

$$\begin{array}{l} CH_2.O.CO.CO.OH \\ | \\ CH.OH \\ | \\ CH_2.OH \end{array} \longrightarrow \begin{array}{l} CH.O.CO.H \\ | \\ CH.OH \\ | \\ CH_2.OH \end{array} + CO_2$$

The oxalic acid added displaces the formic acid from the monoformin, thus:—

$$\begin{array}{l} CH.O.CO.H \\ CH.OH \\ CH_2.OH \end{array} \xrightarrow{\begin{array}{l} CO.OH \\ | \\ CO.OH \end{array}} \begin{array}{l} CH_2.O.CO.CO.OH \\ CH.OH \\ CH_2.OH \end{array} + \begin{array}{l} H \\ | \\ CO.OH \end{array},$$

and the cycle of operations is then repeated.

That this is the correct explanation is shown by the observation that glycerol and oxalic acid interact readily at a temperature below that at which carbon dioxide begins to be evolved, and that, although the acid oxalate which must be formed has not yet been isolated, the products of its interaction with aniline and with ammonia, oxanilic acid and oxamic acid respectively, have been obtained.

That the wh le course of the reaction is as above formulated is rendered practically certain by the fact that a precisely similar cycle of operations can be carried out with ethyl alcohol and oxalic acid when the products can easily be isolated at every stage.

As is well known, ethyl-hydrogen-oxalate, which is formed when ethyl alcohol and oxalic acid are heated together and which can be distilled under diminished pressure, decomposes into carbon dioxide and ethyl formate when heated under ordinary atmospheric pressure, this being the source of the ethyl formate always obtained in such quantity in the ordinary preparation of ethyl oxalate, when the product of heating together oxalic acid and ethyl alcohol is distilled. Oxalic acid heated with ethyl formate displaces the formic acid, producing ethyl hydrogen oxalate.

The more complicated reaction which goes on when glycerol and oxalic acid are rapidly heated together until evolution of carbon dioxide practically ceases, and then at a much higher temperature recommences, and which is always employed for the preparation of allyl alcohol, takes a course which also might have been predicted.

It is possible, though it seems unlikely, that monoformin can decompose to a very limited extent as stated in the text-books, but the chief, if not the sole, source of the allyl alcohol is the normal oxalic ester, dioxalin,

$$\begin{array}{l} CH_2\text{———}CH\text{—}CH_2.OH \\ | \qquad\qquad\quad | \\ O\text{—}CO\text{—}CO\text{—}O \end{array}$$

, which, on heating, splits up into carbon dioxide and allyl alcohol, thus:—

$$\begin{array}{l} CH_2.O.CO \\ | \qquad\quad | \\ CH.O.CO \\ | \\ CH_2.OH \end{array} \rightarrow \begin{array}{l} CH_2 \\ \| \\ CH \\ | \\ CH_2.OH \end{array} + 2CO_2.$$

The presence of this compound in the reaction mixture, after the first evolution of carbon dioxide has ceased, is shown by the production of oxamide or oxanilide when ammonia or aniline is added; these compounds being only thus producible from such a normal ester.

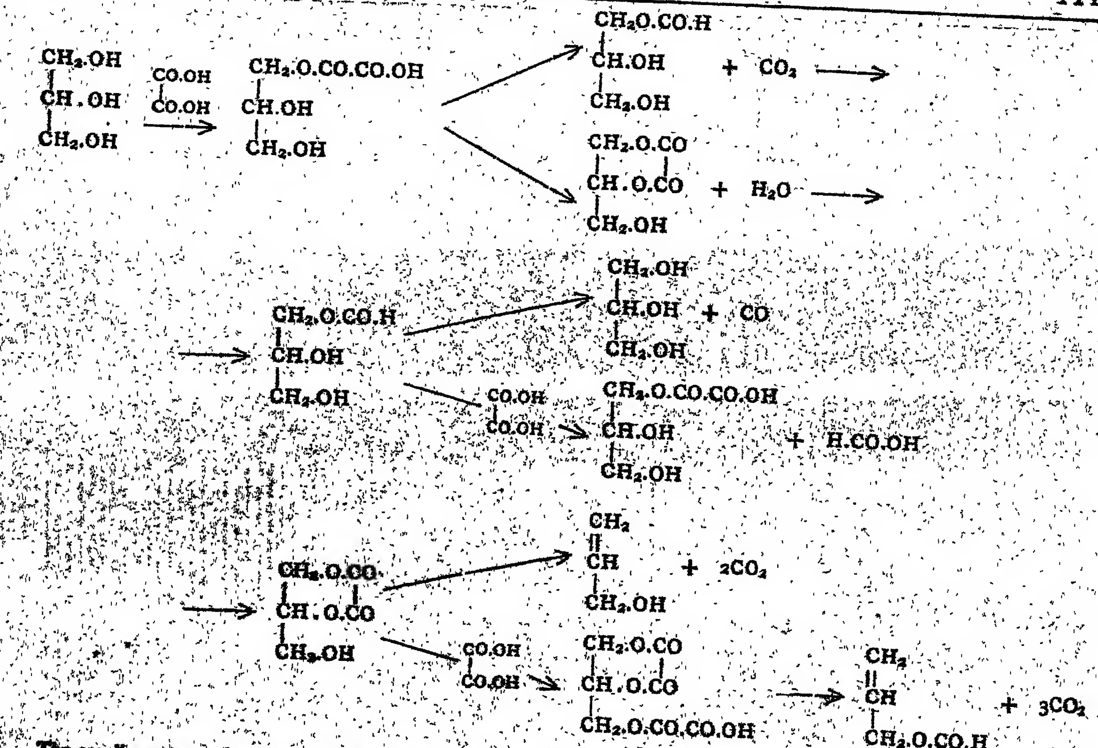
As the quantity of oxamide obtainable always corresponds within the limits of experimental error with the amount of allyl alcohol obtainable, the correctness of this theory of the process is established.

The allyl formate, a little of which is always obtained when allyl alcohol is thus prepared, results from a similar decomposition of oxal-formin, which is produced from monoformin or dioxalin by the further action of oxalic acid, thus:—

$$\begin{array}{l} CH_2.O.CO \\ | \qquad\quad | \\ CH.O.CO \\ | \\ CH_2.O.CO.H \end{array} \longrightarrow \begin{array}{l} CH_2 \\ \| \\ CH \\ | \\ CH_2.O.CO.H \end{array} + 2CO_2.$$

* *Trans.* [illegible]*m. Soc.*, 1914, cv., 151.

† Either [illegible] or the β-hydroxyl group may interact. To save space only the [illegible]ations relating to the former are given here.



The small amount of acrolein and the large quantity of carbon monoxide, which are also formed as by-products in the reaction, result from the decomposition by heat of glycerol and monoformin respectively, the latter yielding carbon monoxide and glycerol, just as formic acid yields water and carbon monoxide when heated.

The main reactions, which take place when glycerol and oxalic acid are heated together, should therefore be formulated as shown in the accompanying scheme.

THE RELATION OF PASSIVITY TO THE PHENOMENON OF ELECTROLYTIC VALVE ACTION.*

By Dr. GÜNTHER SCHULZE,
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PASSIVITY and electrolytic valve action seem to be the most complicated and most difficult of explanation of all anodic phenomena. Many relations between them will be shown best by reviewing the most important features of both.

To begin with electrolytic valve action, we must differentiate between two varieties of it, ionic and the electronic valve action, the latter of which may be further divided into direct-current valve action and alternating-current valve action.

Silver in an aqueous solution of HBr gives an example of ionic valve action. If a current of 3 $\frac{\text{milliamp.}}{\text{cm.}^2}$ is passed through an anode of silver in this solution a smooth black layer is formed on the silver that grows proportional to the amount of electricity passed. After some time the colour of this layer turns to an olive-green. The formation of the layer is accompanied by a proportional rise of the electric tension across it. After a formation of some days with a current of 3 $\frac{\text{milliamp.}}{\text{cm.}^2}$ the layer attained a thickness of 0·85 millimetre, and supported a tension of 400 volts at a current density of 0·2 $\frac{\text{milliamp.}}{\text{cm.}^2}$

The most striking phenomenon of ionic valve action, however, by which it is distinguished both from the electronic valve action and passivity, is that no gas is developed at the anode. The whole amount of current is absorbed in the formation of the solid layer. By increasing the current density it is possible to disrupt the layer, after which all the current passes through the damaged spot and gives rise to a continuous stream of gas bubbles for hours or even days, while the tension at the layer is greatly lowered. But this development of gas is only an apparent exception to the given phenomenon, as it interrupts the formation.

If the current through a formed silver anode is reversed valve action appears. The tension, high at the first moment, drops almost instantaneously to a low value. If the original direction of the current is restored the tension is low at first, but regains its former amount very quickly. These changes of tension, however, are quite unable to follow the oscillations of an alternating current of 50 periods a second, and in consequence there is not the slightest sign of rectification of such a current by a silver anode in hydrobromic acid.

It is easily understood that all these phenomena are caused by the various resistances the different ions find in the layer of silver bromide. As the time the ions take to pass the layer is large compared to 0·01 second, ordinary alternating current cannot be rectified.

Ionic valve action occurs further with silver in HCl and HI and with copper in HF.

Electronic valve action shows quite different and much more intricate features. Aluminium, the first valve metal known, may serve as a first instance for their description.

* A Contribution to the General Discussion on "The Passivity of Metals" held before the Faraday Society, November 12, 1913.

If aluminium in a suitable electrolyte, such as a solution of $Na_2B_4O_7$, is made the anode of a constant direct current, there is both oxygen developed and a solid skin of aluminium oxide formed at its surface. At first this solid skin is so extremely thin that it is invisible. After some time it appears as a whitish-grey film of a hard, almost crystalline structure that is pierced by innumerable pores of microscopic size. The formation of this solid film absorbs only about 5 per cent of the whole current available. The rest of it develops free oxygen that escapes.

Thus the valve metals show quite the same strange phenomenon as the passive metals, viz., anodic rise of oxygen from a metal that combines with it very readily in the ordinary state.

Taking H_2SO_4 as electrolyte we find this still more obvious. Iron as well as aluminium form easily soluble compounds with it, whereas when used as anodes and loaded with a sufficient current density neither dissolve, but oxygen is set free at their surface. In the case of aluminium the phenomenon is still more puzzling than with iron, as aluminium combines very violently with oxygen. In air it only seems to be inactive because it protects itself from the oxygen by a continuous, impermeable skin of aluminium oxide, which momentarily covers every scratch made on an aluminium surface and is at first of little more than molecular thickness. By diffusion of oxygen through it, it grows very slowly. When its formation is made impossible, as by amalgamating the aluminium with mercury, a stormy reaction of the aluminium with the oxygen of the air takes place at once, and strangely shaped dendrites of aluminium oxide grow quickly and steadily out of the amalgamated surface. And for all that even nascent oxygen is set free from aluminium surfaces in H_2SO_4.

Before we try to explain this fact we must lay stress upon the most important difference between passive metals and valve metals. It is still open to discussion whether passivity is caused by a layer of oxide or not, but if there is such a layer it possesses metallic or electronic conductivity. Thus it serves as an anode instead of the metal it covers, and there is no reason why it should grow much beyond molecular thickness.

The oxide skin on the valve metals, on the contrary, insulates very perfectly. In consequence it cannot serve as an anode, but only as an obstacle that is constantly pierced by the ions and constantly regenerated by chemical action. Thus the film grows proportional to the time the current is flowing and gives rise to the following various phenomena which are completely absent from passive anodes.

The first is the rise of tension at the valve anode, that is also proportional to the time of formation until it reaches a well defined point, at which innumerable fine sparks become visible at the anode. This point is called sparking voltage. Beyond it the tension decreases to a second definite value, the maximum voltage, which, with a given combination of valve metal and electrolyte, cannot be exceeded. If, on the other hand, not the current but the tension is kept constant at a value that lies below the maximum voltage, the current continually decreases and soon reaches extremely small values. Then the "effective layer" upon the anode has a resistance of many megohms and may be regarded as the dielectric of an electrostatic condenser, whose electrodes are formed by the valve metal on one and the electrolyte on the other side. The capacity of this condenser is easily measured and found surprisingly large. Furthermore, it is almost inversely proportional to the tension at which the valve metal is formed independent of the nature and concentration of the electrolyte used, at long as aqueous solutions are employed. For each valve metal, however, and every non-aqueous solvent it has a different characteristic value. One square centimetre of an aluminium anode formed at 100 volts in aqueous solution has a capacity of 0·08 microfarad. From this capacity the thickness δ of the effective layer might be calculated if the dielectric constant ϵ of this layer were known. As it has not been possible yet to measure it, we must be content to calculate the relative or reduced thickness δ/ϵ by simply assuming $\epsilon = 1$. According to the behaviour of the capacity of the effective layer stated above its thickness δ/ϵ is nearly proportional to the forming voltage and a characteristic function of each valve metal. The reduced thickness of the effective layer upon an aluminium anode formed at 100 volts in an aqueous solution amounts to 0·000010 millimetre.

At first sight it might be supposed that "effective layer" and solid oxide skin were identical, but a research as to the thickness of the latter shows that this supposition is wrong. As the oxide film is much too thin to ascertain its thickness mechanically, it must be measured in the same way as the effective layer, viz., by measuring its electrostatic capacity. The oxide film must be made the dielectric of a condenser. For this purpose it is carefully rinsed with distilled water in order to free it from the last traces of the electrolyte and carefully dried, whereupon the cell is filled with mercury instead of the electrolyte. Thus we have a condenser whose conductors are aluminium and mercury, and whose dielectric is formed by the whole thickness of oxide film. By measurements of this kind it was found that the effective layer which causes all the phenomena of the valve action and the solid oxide film are entirely different phenomena, which must be sharply distinguished. While, as stated above, the thickness of the effective layer of a given valve metal is only dependent on the forming voltage as long as aqueous solutions are used, the thickness of the solid oxide film is not always much larger than that of the effective layer, but depends also on the nature and concentration of the electrolyte and its temperature, the density of the forming current, and may even in certain cases grow continuously, while forming voltage and thickness of the effective layer are maintained at a constant value. Thus the effective layer must be something essentially different from the oxide film, and it is hardly imaginable that it can be anything else but a gas layer within the microscopic pores of the solid film.

Thus I was led to adopt the following view of the different layers at a formed valve metal's surface and of the processes which originate it.

δ' in Fig. 1, which gives a greatly magnified diagrammatic scheme of the layers, is the whole of the solid oxide skin and consists of the following parts:—

1. α, the *continuous* oxide skin of molecular thickness that always covers aluminium surfaces.

2. β, the gas layer within the pores of the *porous* oxide film.

$\alpha + \beta = \delta$ is the "effective layer." As α is very small relative to β it may be neglected and δ simply be called the gas layer.

3. γ, the part of the solid porous film whose pores are filled with the electrolyte. Its resistance is a good deal larger than that of the electrolyte, but may be neglected when compared with the resistance of the gas layer.

These different layers seem to arise in the following way. If a newly polished aluminium anode is immersed in the electrolyte, it is covered with the layer α, which insulates, but for its molecular thickness can withstand only very small tensions. It is obvious that as soon as the current is closed the layer α will be pierced everywhere by the incoming ions, or rather an easily derivable part of them, the oxygen. The oxygen ions having passed the layer and reached the aluminium transfer their charge to it and form a new oxide film below the original, which is disrupted again by new ions, thus forming a thicker porous oxide skin.

But how does the gas layer form, and why does the greater part of the oxygen escape?

The only possible explanation of this seems to be the assumption that most of the oxygen ions do not reach the aluminium itself but give up their charge, the negative electrons, when they encounter an obstacle of high

resistance and in consequence a high potential gradient, and that the freed electrons only pierce the resisting layer.

The places at which the oxygen ions encounter an extremely high resistance are the junction between gas layer and electrolyte as well as the junction between gas layer and the solid continuous film a. Let us suppose that the greater part of the oxygen ions lose their electrons when they arrive at the junction between electrolyte and gas layer. The electrons fly to the aluminium and the neutralised oxygen atoms escape out of the oxide skin, as they get a heavy impact by their separation from the electrons. The small number of oxygen ions which did not give up their electrons at that limit, because it just was in an oscillatory state that prevented the electrons from escaping, passes the gas layer and arrives at the second junction between the gas layer and the solid film a. Here the same will happen as

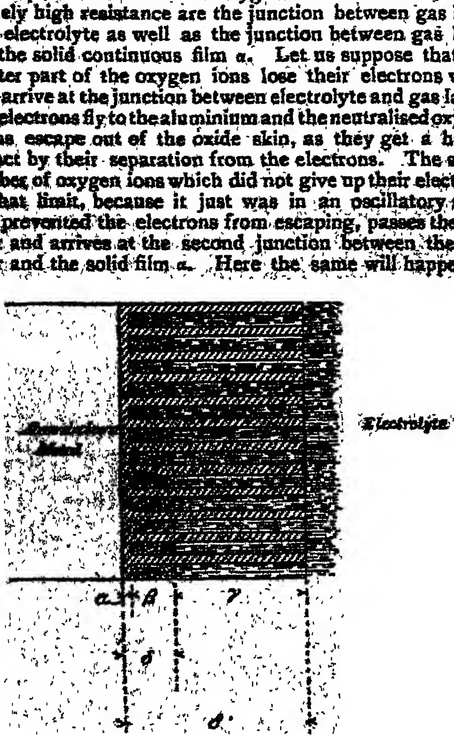


FIG. 1.

at the first junction. Most of the ions will lose their electrons, a few, prevented from doing so by their momentary (oscillatory) state, will pierce the solid film a, oxidise the aluminium, and reinforce the oxide film. The oxygen ions which are neutralised at this second limit cannot escape, but cause the growth of the gas layer.

It would lead us too far to show how all phenomena of valve action can be explained by means of this scheme.

Another classification of valve action, which has its analogy in passivity, is that of complete and incomplete valve action. When a valve metal is insoluble in the electrolyte it shows complete valve action. Tantalum behaves like that in almost all electrolytes. In contradistinction to it the valve action becomes more incomplete the more the valve metal is soluble in the electrolyte. Aluminium shows many instances of it. The characteristics of incomplete valve action are:—The forming current does not converge to zero when the voltage is kept constant, but to a constant value, which is higher the more the valve metal is soluble. The maximum voltage cannot be reached, but the formation stops at a lower voltage. Aluminium in dilute sulphuric acid, *e.g.*, can only be formed at 20 volts instead of 400, which would be reached if the valve action were complete. The forming current must exceed a minimum value before formation sets in. After breaking the current the valve action disappears again.

Most of these features are also shown by iron becoming passive in dilute sulphuric acid; a marked solubility, a minimum current for starting the passivity, its disappearing after breaking the current. On the contrary, iron in concentrated HNO_3 shows complete passivity.

The performance of the valve metals as cathodes is best seen by taking oscillograms of the alternating current and voltage applied to a valve cell. As mentioned before, we must distinguish between direct-current valve action and alternating-current valve action. To which of these a cell belongs does not depend on the valve metal only but also on the electrolyte. The combinations with direct-current valve action show all the described phenomena as long as the valve metal remains anode, but the moment the current is reversed the valve action is destroyed and the cell must be re-formed from the beginning, when the valve metal is made the anode again. Alternating current is not rectified, but passes the cell unhampered in both directions.

Combinations with alternating current valve action rectify alternating currents up to the highest frequencies. Between both there are many intermediate states. Bismuth, antimony, cadmium, and zinc are valve metals which show d.c. valve action in aqueous solutions. The reason is obvious. Their oxide films are reduced by the cathodic hydrogen. In pure sulphuric acid they rectify alternating currents, as the skin formed in this electrolyte seems to consist of the sulphate instead of the oxide and is not reduced by the hydrogen.

Here we find another relation to the behaviour of passive metals. Their passivity is also destroyed by hydrogen developed on them in the cathodic direction of the current. But this seems to be the case with all passive metals. The analogy to alternating-current valve action is missing; no passive metal combines so vigorously with oxygen that the compound may withstand reduction. This may be explained by the fact that if the oxide-film theory is correct, tantalum, the *non plus ultra* of alternating-current valve action, is unable to rectify alternating currents in solutions of $AuCl_3$ and $PdCl_2$, as the current in its cathodic direction deposits gold or palladium at the tantalum. To dissolve it again the same amount of electricity is wanted in the anodic direction, and the valve action is made ineffective. Other cations are only partly deposited, so that a part of the valve action survives. Fig. 2 shows this clearly. It is an oscillogram of an alternating current and voltage of the frequency 50 applied to tantalum in an aqueous solution of $Cu(NO_3)_2$, 0·2 normal; a is the current through the cell, b the tension at its connections. The surface of the tantalum was 2 cm.².

At the point b the tantalum becomes cathode. The current remains zero until the voltage has reached the point c; also in the cathodic direction there is a minimum potential that must be surpassed before the current through the effective layer can start. While it flows and deposits copper on the tantalum the voltage is almost constant at first, and decreases to zero, together with the current thereafter. At d the tantalum becomes anode; but as there is copper deposited on it, it behaves like an ordinary copper anode up to the point e, where the current suddenly drops to nearly zero and the voltage rises to its normal valve value. It is obvious that when the current has reached the point e all the copper deposited before on the tantalum has been consumed and the valve action is re-established. Thus only a part of the current flowing in the cathodic direction has deposited effective copper; the rest must have developed hydrogen or deposited copper in a state in which it could not serve as anode. The cations Cd, Ag, Zn, Pb, Fe, Tl act in the same way with decreasing effect along the row. With all other cations, especially with Bi, Hg, Cr, Mn, Co, Ni, tantalum shows undisturbed alternating valve action, for which the oscillogram Fig. 3 may serve as paradigma. It was taken from a cell with tantalum in an aqueous solution of KNO_3, 0·5 normal.

V is the voltage of the open circuit. The other points are easily understood on account of their likeness to Fig. 2.

The only phenomenon I want to lay stress upon is that the current a becomes zero at d, that is, before the voltage has disappeared. That proves that there is also a minimum potential below which the current cannot subsist, analogous to the electric arc for instance.

In the anodic direction the current through the cell is zero from the beginning. The small current shown in Fig. 3 does not pass the effective layer, but is the charging current of the high electrostatic capacity of the layer, as is

sufficiently shown by the fact that it is shifted through 90 degrees against the voltage.

This phenomenon, that the current is zero from the beginning, is important for the theory of valve action. If valve action were caused by a partial destruction of the oxide film in the cathodic direction and a reforming of it in the anodic, as some authors formerly held, or by some kind of diffusion different in both directions, there must at all events be a re-forming current through the cell in the beginning of each anodic period. That there is none is a conclusive proof for the supposition that the effective layer is not changed by the cathodic direction of the current and that valve action cannot be explained by diffusion—in short, that it is not an ionic but an electronic phenomenon.

Summarising the essentials of valve action from the statements above we may say:—There is a defined high anodic and a defined low cathodic voltage, which must be

dissolve chemically in acids and anodically in electrolytes, behave differently in some cases. When dipped in certain strong acids they do not dissolve, and when made anodes in corresponding electrolytes they develop oxygen instead of forming ions. Some of them are passive in all electrolytes, others only in some cases. The latter may be subdivided into those which are passive without the aid of an anodic current and those which turn from the active into the passive state only when the anodic current is strong enough. Iron in dilute HNO_3 or H_2SO_4 is an instance of the last type. When the iron has entered the passive state the current may be lowered a good deal below the amount at which the passivity arose before the ions become active again. Increasing temperature decreases the passivity, cathodic hydrogen destroys it.

Some authors have found that passive anodes possess a very great electrostatic capacity, and have concluded that they were covered by an oxide film. Other authors have

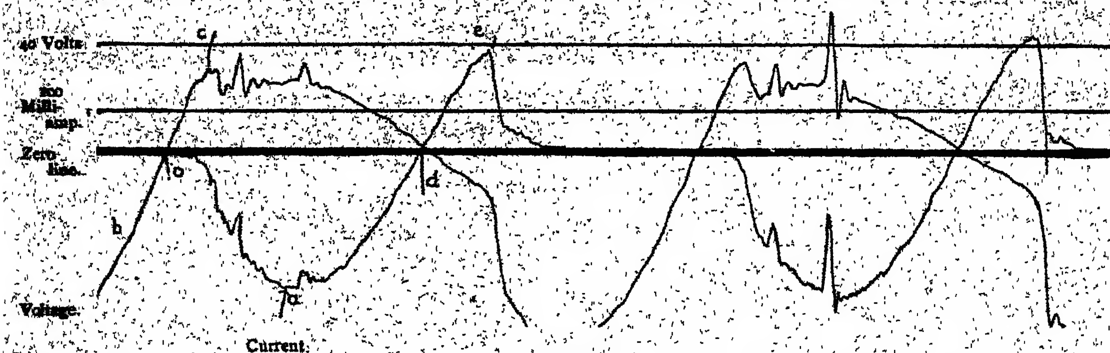


FIG. 2.

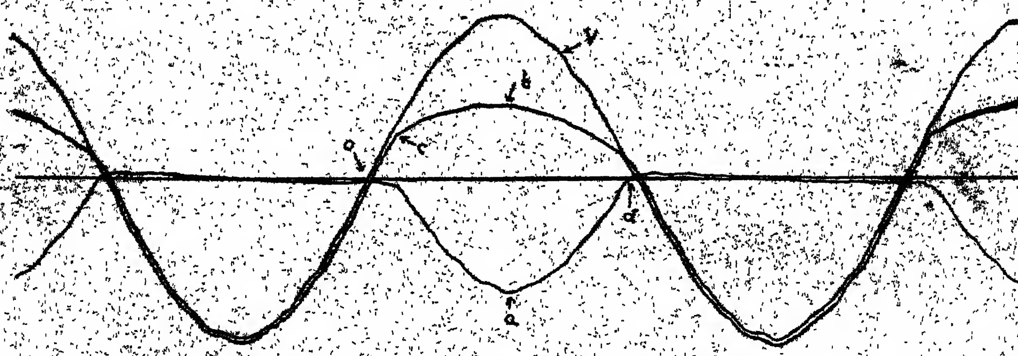


FIG. 3.

exceeded before a current can flow through a valve electrode. The first is identical with the voltage at which the valve metal is formed, the second is the "minimum potential."

That the anodic voltage is high was explained above by the assumption that electrolytic anions must be subjected to a high potential gradient ere they lose their electrons, which in this case are bound to non-metallic atoms. In the same way the low cathodic voltage may be explained by the supposition that a relatively low potential gradient suffices to free the electrons from the valve metal. Thus the electronic valve action is caused by the different forces with which the non-metallic (electronegative) atoms and metallic (electropositive) ions bind the electrons.

The phenomena of passivity have been partly mentioned in the above. In the following only the most important of them will be summarised. Some metals which would be expected according to their position in the electrochemical series and to their general chemical behaviour to

put forward more reasons for such a film, but its existence did not remain unquestioned.

As I have not worked myself on passivity it is not for me to take a part in this controversy. The only thing I wish to point out is the remarkable analogy between the phenomena of valve action and passivity which follows from the assumption that valve action is caused by an *insulating* film and consequently a gas layer, while passivity takes place if the film shows metallic (electronic) conductivity together with a limited or negligible solubility in the electrolyte.

The consequence of the metallic conductivity of the film is that it cannot grow much above molecular size and must be almost undetectable by optical or mechanical means. The oxygen developed at its outer surface covers it more or less and protects it against the electrolyte when it has been formed. Thus the current may be decreased below the critical forming value without restoring activity.

The behaviour of iron in H_2SO_4 of different concentra-

tion is of special interest. In dilute sulphuric acid it shows passivity, in concentrated acid valve action. In intermediate concentrations an unstable valve action is succeeded by stable passivity. In dilute solutions the anion SO_4 may form an oxide of iron by the aid of the water. In concentrated solutions the small amount of water present is not available for this reaction, as it is bound to the sulphuric acid itself. Therefore ferric sulphate must be formed. This insulates and causes valve action.

Therefore I hold:—Valve action is caused by an insulating skin of ultra-molecular thickness with a thin gas layer within it; passivity by a conducting skin of molecular thickness with a molecular gas layer upon it.

THE SCIENTIFIC WEEK.

(From Our Own Paris Correspondent).

DISEASE OF TIN.

Very curious researches on the density of tin at different temperatures have recently been made by M. Pascal. They have been communicated to the Academy of Sciences by M. Henry Le Chatelier. In a solid state tin possesses three allotropic varieties; in a liquid state it presents an allotropic variety like sulphur. The disease or pest of tin, as it has been called by the learned Dutchman Ernst Cohen, seems to be constituted by one of these allotropic varieties. This sick tin, spotted with grey pulverulent spots, has a density inferior to about 15 per cent to that of normal tin. The metal has undergone, as it were, a swelling followed by a molecular disaggregation. The third allotropic variety is distinguished by a somewhat different crystalline structure.

NEON TUBES AND THE AURORA BOREALIS.

The origin of the Aurora Borealis still remains mysterious; nevertheless, a very ingenious explanation has just been given to the Academy of Sciences by M. George Claude in a paper presented by Prof. d'Arsonval. M. Claude has noticed that the difference of potential at the limits of neon tubes decreases to a half, third, or quarter of the ordinary value when the diameter of the tube doubles, triples, and quadruples, so that very small voltages would suffice to work enormous tubes. Besides the practical consequences of such a state of things from a lighting point of view, this observation, as Prof. d'Arsonval suggests, brings with it the explanation of one of the most interesting physical problems of the globe. If, indeed, the results of M. Claude are applicable to other gases of the globe, the magnificent Aurora Borealis, which are but the electrical discharges of nebulous action, would only require differences of potential far inferior to what might be thought necessary and the existence of which was difficult to understand.

GRADUAL COOLING OF THE EARTH.

M. Appel, President of the Academy of Sciences, at the last sitting of the assembly, presented an important work by M. Verona on the gradual cooling of the earth. At the same sitting M. Andrade presented a paper on a new method of compensation of chronometrical apparatus. M. Roux, director of the Pasteur Institute, also made a new communication from MM. Fillat and Jonassier concerning the training of microbes in suspension in water under the influence of a draught. These authors have already shown that the superficial tension of the liquid has a more or less great influence on this action. Their recent works show that the nature of the microbe and its age likewise have an influence on the evolution of the phenomenon.

RÔLE OF INSECTS IN THE TRANSMISSION OF DISEASES.

Numerous diseases are transmitted by stinging insects. This is the case for yellow fever, which is spread by the *stegomya*; the sleeping sickness, also, is propagated by the tsé-tsé flies, &c. But besides these mosquitoes and flies, fleas would seem to play a very important rôle in the progagation of the deadly diseases. Experimental researches have just been made at the Pasteur Institute on the part played by these insects in trypanosomiasis. Their rôle is henceforth distinctly determined. The fleas that bite infected animals are contaminated, and in their turn they transport the microbian agent on to other animals that they may happen to sting.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, February 19, 1914.

SIR WILLIAM CROOKES, O.M., President, in the Chair.

BY invitation of the President, Prof. MAX WOLF exhibited a series of slides of Nebulæ, from the Observatory of Heidelberg.

Papers were read as follows:—

"*The Brain of Primitive Man, with Special Reference to the Cranial Cast and Skull of Eoanthropus ('the Piltdown Man').*" By Prof. G. ELLIOT SMITH, F.R.S.

An account is given of the difficulties that present themselves in any attempt to reconstruct "the Piltdown skull" from the few damaged fragments that have been recovered, and attention is called to a large series of points of anatomical detail which indicate the only way in which these difficulties can satisfactorily be circumvented.

The cranial cast obtained when thus correctly reconstituted is compared with those obtained from the calvaria of *Pithecanthropus*; the Monsterian series of crania (especially those found at Neanderthal, Gibraltar, La Chapelle-aux-Saints, and La Quina); those representing Aurignacian and later times; and a number of cranial casts and actual brains of primitive types of modern men and apes.

The results go to prove that the small brain of *Eoanthropus*, though definitely human in its characters, represents a more primitive and generalised type than that of the genus *Homo*. Nevertheless, it can be regarded as a very close approximation to the kind of brain possessed by the earliest representatives of the real *Homo*, and as the type from which the brains of the different primitive kinds of men—Mousterian, Tasmanian (and Australian), Bushman, Negro, &c., no less than those of the other modern human races have been derived, as the result of more or less well-defined specialisations in varying directions.

From the features of its brain *Pithecanthropus* must be included in the family Hominidæ, but it and *Eoanthropus* can be looked upon as divergent specialisations of the original genus of the family. *Pithecanthropus* represents the unprogressive branch which survived into Pleistocene times before it became extinct; *Eoanthropus* the progressive phylum from which the genus *Homo* was derived.

Special attention is devoted to the study of the temporal region of the brain, which in all of these fossil men (not excluding *Pithecanthropus*) reveals features of great morphological interest. The opinion is expressed that the increased size of the brain (as a whole) which is distinctive of the Hominidæ, among the Primates, is intimately related to the acquisition of the power of articulate speech, and that the very earliest representatives of the family must have possessed in some slight degree the definite faculty of inter-communication one with another by means of vocal sounds. The development of asymmetry of the brain was necessarily incidental to the acquisition of human characteristics, and must have been already present in the original Hominidæ.

"*Oxidases.*" By Prof. A. J. Ewart.

"*New Malarial Parasite of Man.*" By J. W. W. Stephens, M.D.

"*Investigations Dealing with the Phenomena of 'Clot' Formations.* Part II. *The Formation of a Gel from Cholate Solutions having many Properties Analogous to those of Cell Membranes.*" By S. B. Schryver.

"*Influence of the Position of the Cut upon Regeneration in* Gunda ulvæ." By Dorothy Jordan Lloyd, B.Sc.

CHEMICAL SOCIETY.

Ordinary Meeting, February 5, 1914.

Prof. W. H. Perkin, LL.D., F.R.S., President, in the Chair.

(Concluded from p. 104).

37. "*A Criticism of Holmes' Method of Determining the Molecular Complexity of Liquids.*" By William Ernest Stephen Turner.

In a recent paper (*Trans.*, 1913, ciii., 2147), and in continuation of previous work (*Trans.*, 1906, lxxxix., 781; Holmes and Sageman, *Trans.*, 1907, xci., 1608; 1909, xcv., 1919), Holmes sets out the results of a method which he employs for the determination of the molecular complexity in the liquid state. As a new method of attacking an old problem it deserves a welcome, but the results are so much different from those deduced on the basis of other and well-known methods that they call for examination.

The view adopted by the author of the theory is that in most cases the only forces which are brought into action when two liquids mix are of a physical character, and that the miscibility of liquids depends on the true relative molecular volumes, or what comes to the same thing, the relative radii, of the constituents. The method employed to obtain the relative complexities is, therefore, to determine the molecular composition, referred to the gaseous state, of the liquid mixture in which the maximum deviation occurs between the calculated and observed proportions by volume of the constituent with the larger molecular volume. The ratio of the molecular proportions so obtained is considered as that of the relative molecular complexities, water, for example, from its mixture with ethyl tartrate being considered to have a molecule, $(H_2O)_4$, relative to the ester; and by similar processes, molecular formulæ $(C_4H_{10}O)_4$, $(CHCl_3)_8$, $(C_6H_6)_8$, $(C_6H_{14})_8$, and $(CS_2)_{16}$ are assigned. In practice, however, the method is not so simple as it appears; thus, the mixtures of maximum deviation in the case of water with ethyl and propyl alcohols are $C_2H_6O,1\frac{1}{4}H_2O$ and $C_3H_8O,2\frac{1}{4}H_2O$ respectively, and of water and *n*-butyric acid, $4C_4H_8O_2,7H_2O$; yet the alcohols and butyric acid are nevertheless held to be of a similar complexity to water, in order to agree with the author's theory that molecular radii must have certain values to permit of miscibility. Nor are substances of approximately equal molecular volume, like aniline and ethyl acetate, soluble in water to anything like the same extent, and to explain this discrepancy, speculations are introduced concerning the quasi-electrical forces which are presumed to act, causing disturbances in the molecular volume or co-volume.

Without dealing further with these speculations, however, it may be said that the results themselves are sufficient evidence of the antagonism between this method and those based on current physico-chemical doctrines. The main points to be noted about the values of the degree of complexity given by Holmes are that (1) they appear to vary from substance to substance by the factor 2, being 1, 4, 8, or 16; (2) they are represented by integral numbers; (3) the substances which all others methods demonstrate to be normal are often the most associated of all.

Now the occurrence of whole numbers as association factors must have a definite meaning. In a gas the molecules of which are capable of association there is at any temperature a condition of equilibrium between two sets, the more and the less complex molecules, this equilibrium being readjusted at each alteration of temperature. With sulphur vapour, according to the conditions of temperature and pressure, molecules S_8, S_6, S_2, and S_1 exist, three forms often co-existing (Preuner and Schupp, *Zeit. Phys. Chem.*, 1909, lxviii., 129). There is no *a priori* reason to suppose that in the liquid state an associated substance can have but one degree of complexity independent of temperature; indeed, it would be surprising if the general effect of temperature and pressure was entirely different for different states of matter. The case of nitrogen peroxide may be quoted against such a possibility; for as liquid nitrogen peroxide becomes coloured with rise of temperature, it must of necessity indicate that a different molecule is being produced, almost certainly NO_2, since the substance of this formula has a brown colour in the state of vapour; thus, without any assumption either as to the distribution of kinetic energy added to a substance, or of the actual molecular complexity, the behaviour of nitrogen peroxide clearly shows that the degree of aggregation of a liquid is certainly affected by temperature variation. If Holmes's theory is correct, however, then it is most improbable that temperature has such an effect. Holmes himself admits this (*Trans.*, 1913, ciii., 2164), for if the degree of complexity can be represented as a whole number in every one of the twenty-seven examples given, then it is highly improbable that either of the constituents of a liquid can have present within it molecules of two or more degrees of complexity, such as one must presume to exist on the consideration of the non-integral values derived by the Ramsay and Shields' method and its numerous modifications, or Traube's or Guye's or any other method depending on the study of properties very varied in character; and the improbability is all the greater when it is remembered that Holmes's numbers are derived from measurements made at purely arbitrary temperatures at which the liquids are far from being at corresponding states.

Again, the degree of complexity deduced by the method appears to be independent of the nature of the second component of the mixture, for the value arrived at is the same; for example, when ethyl alcohol is mixed with water, or with ethyl ether, methyl iodide, or carbon disulphide, results wholly at variance from those obtained by freezing-point and boiling-point measurements, which indicate that the nature of the solvent is a powerful factor in modifying molecular state (compare Auwers, *Zeit. Phys. Chem.*, 1899, xxx., 300; Meldrum and Turner, *Trans.*, 1908, xciii., 876; 1910, xcvii., 1605; Turner, *Trans.*, 1911, xcix., 880).

The third point mentioned above is equally important. Against the probability that *n*-hexane, benzene, and carbon disulphide are associated in the way Holmes believes, there is much evidence from a consideration of several properties. It would, for example, not be easy to reconcile the great complexity of $(CS_2)_{16}$, of molecular weight 1216, with a boiling-point as low as 46°. There are, however, more fundamental objections. Consider the substances ethyl ether, ethyl acetate, benzene, *n*-hexane, chloroform, and carbon disulphide, all of which Holmes considers so complex. In the state of vapour they each occupy a volume corresponding with the simplest possible molecular formula, and if, therefore, any alteration of complexity occurs, it must be presumed to take place when the vapour condenses. If, therefore, the temperature of the mixture of liquid and vapour be raised towards the critical point, either the molecular complexity of the liquid must decrease (which on Holmes's view is improbable, as shown above) or that of the vapour must increase, since liquid and vapour become identical at the critical point. Now when vapour and liquid are of different degrees of complexity, it has been found (Young, *Phil. Mag.*, 1892, [5], xxxiv., 503; Young and Thomas, *Trans.*, 1893, lxiii., 1191; Young, "Stoichiometry," Long-

mans, 1908; compare Ramsay, *Proc. Roy. Soc.*, 1894, lvi., 171) that the various critical relationships are abnormal. Water, the alcohols, and acetic acid, all of which Holmes agrees are associated, are abnormal; but benzene, *n* hexane, ether, ethyl acetate, and alkyl iodides are not, and one may conclude that the complexity of the liquid and vapour undergoes little or no change. Similarly, it is possible from the value of the surface tension of a liquid at the ordinary temperature (Ramsay and Shields, *Trans.*, 1893, lxiii., 1089) or from the viscosity (Batschinski, *Zeit. Phys. Chem.*, 1911, lxxv., 665) to calculate with a fair degree of accuracy the critical temperatures of benzene, ether, ethyl iodide, ethyl acetate, and carbon disulphide, whereas with the unquestionably associated substances this is quite an impossible matter.

In conclusion, it may be pointed out that Holmes's results are deduced from solutions, and not from the pure liquid itself, in which case, despite the strength of solution used, there should be at least some measure of comparison between his results and those derived from methods based on osmotic-pressure determination. Actually, results of an opposite character are found, hydrocarbons and their halogen derivatives, ethyl acetate, carbon disulphide, &c., to which Holmes assigns a high degree of complexity, being quite unassociated by freezing-point and similar tests. It therefore follows from what has been said, that if Holmes's method is correct, temperature has no effect on the degree of complexity of a liquid; and present interpretations of critical data, as also van 't Hoff's laws of solution, are untenable. If, on the other hand, they are correct, Holmes's deductions cannot be. In the author's opinion, Holmes's numbers cannot represent the molecular complexities of liquids, either actual or relative.

38. "*Phytin and Phytic Acid.*" By GEORGE CLARKE.

A detailed description of work of which a preliminary account has already appeared (*Proc.*, 1913, xxix., 27).

39. "*Sulphonyl and Carbonyl Derivatives of Aniline. Resolution of Externally Compensated* p-*Toluenesulphonyl alanine into its Optically Active Components.*" (Preliminary Note). By CHARLES STANLEY GIBSON.

In continuation of the work of Pope and Gibson (*Trans.*, 1912, ci., 939), a comprehensive stereochemical study of derivatives of aniline and other amino-acids is being undertaken.

The method of preparation of externally-compensated *p*-toluenesulphonylalanine has been conveniently modified, and the compound has been resolved into its optically active components by the method of Pope and Gibson (*loc. cit.*),

One equivalent of *p*-toluenesulphonylalanine was treated in boiling aqueous solution with half an equivalent each of strychnine and sodium hydroxide, and after allowing the clear solution to remain, an almost theoretical quantity of the strychnine salt of *d p*-toluenesulphonylalanine separated. This was re-crystallised from very dilute alcohol, and obtained in clusters of colourless needles, melting at 188—189°. The acid remaining in the mother-liquor from the separation of the strychnine salt was then isolated, and treated with the corresponding quantities of brucine and sodium hydroxide in boiling water. After some time a good quantity of the brucine salt of *l-p*-toluenesulphonylalanine separated. This was re-crystallised from a large quantity of boiling water, and obtained in long colourless prisms, melting at 148—149°.

d-p-*Toluenesulphonylalanine*,—

$$CH_3\cdot CH(CO_2H)\cdot NH\cdot SO_2\cdot C_6H_4\cdot CH_3,$$

was obtained in the usual manner from the strychnine salt, and after one recrystallisation from aqueous alcohol it was found to be pure, and separated in long colourless needles, melting at 131—132°. Its rotation was determined in alcoholic solution at 25°.

0·5894, made up to 25 cc. and observed in a 2-dcm. tube, gave a_D +0·37°, $[a]_D$ +7·71°.

In a similar way l-p-*toluenesulphonylalanine* was isolated from the brucine salt, and this was obtained pure after two recrystallisations from aqueous alcohol. It appeared in well-defined colourless crystals, melting at 131—132°. The melting-point of the racemic compound is 138—139° (*loc. cit.*). The rotation of the lævo-compound was determined under the same conditions as the above:—

0·5472 gave a_D −0·35°, $[a]_D$ −7·62°.

The completion of this and other investigations is being delayed so that the final observations may be made under better and more accurate conditions.

40. "*The 'Azeotropic' Mixtures of Ethyl Acetate and Water.*" By ROBERT TABOR LATTEY.

Although its derivation signifies "unchanged by boiling," Wade defined an azeotropic mixture as one of maximum (or minimum) boiling-point. The mixtures of ethyl acetate and water described by Merriman (*Trans.*, 1913, ciii., 1798) do not strictly fall under this definition. The points representing their composition and pressure on a P/*x* diagram are three—two for liquid phases and one for vapour phase. None of these is a maximum point; that representing the vapour phase is the intersection of two curves. This was pointed out in the case of triethylamine and water, where similar conditions prevail (*Trans.*, 1907, xci., 1959). It is not possible to construct the complete P/*y* curve (y = molecular fraction of water in vapour) from Merriman's data, but its correct form at 37·55° is shown in the accompanying figure. The right-hand branch cannot have the form assigned to it by Merriman, since $p_2 = y$P by definition and p_2 is very nearly constant for the water-vapour in contact with its solutions in ethyl acetate at each of the temperatures investigated.

For a true azeotrope, $\frac{dP}{dy} = 0$. In the case of ethyl acetate and water, $\frac{dP}{dy}$ has two values for the vapour in contact with mutually saturated solutions. At 37·55° these are given by the two values of—

$$\frac{y - x}{y(1-y)}\text{P},$$

namely,

$$\frac{0{\cdot}231 - 0{\cdot}169}{0{\cdot}231 \times 0{\cdot}769}\text{P and } \frac{0{\cdot}231 - 0{\cdot}986}{0{\cdot}231 + 0{\cdot}769}\text{P} = +70 \text{ and } -850,$$

using Merriman's data.

There is a hypothetical azeotrope in this case having the composition $x = y = 0{\cdot}25$ (approximately). This cannot be realised, since the liquid separates into two layers. The horizontal line in the figure indicates the composition at A and B of the saturated liquid phases, and at C of Merriman's so called "azeotrope." Liquid and vapour cannot co-exist under conditions indicated by points above the line ACB. For, suppose a solution were prepared having $x >$ that corresponding with the point A, for example, $x = 0{\cdot}18$, the vapour corresponding with this liquid would have a composition between $y = 0{\cdot}23$ and $y = 0{\cdot}25$, and exert a pressure of about 205 mm. Such a vapour is saturated at about 194 mm., and would, therefore, undergo partial condensation. Distillation would therefore go on until two liquids, A and B, had formed.

The second (hypothetical) maximum at about $x = 0{\cdot}85$ does not indicate an azeotrope. It is true that—

$$\frac{dP}{dy},\ \frac{dp}{dx},\ \text{and}\ \frac{dp_2}{dx}$$

are all zero. It is, however, not necessary that $\frac{dP}{dx}$ shall also be zero, and hence—

$$y = x \cdot \frac{dP}{dy}$$

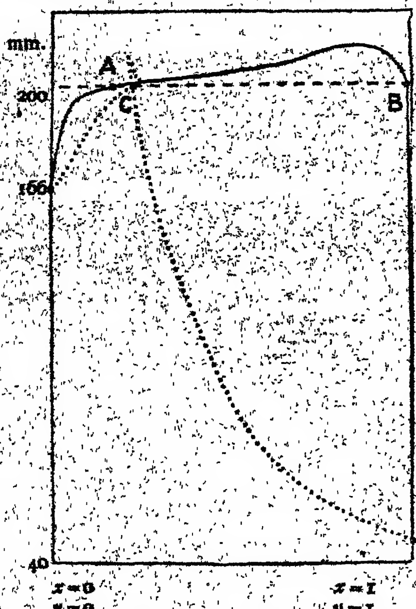
does not change signs here, since both dP and dy change signs. If the following forms of the equation deduced by Duhem, Margules, and Lehfeldt are examined:—

$$\frac{dP}{dy} = \frac{y - xP}{y(1-y)} \text{ and } \frac{dp_2}{dy} = \frac{1-x}{1-y}\text{ P and } \frac{dp_1}{dy} = -\frac{x}{y}\text{P},$$

it is seen that (i.) if $y = x$ the total and partial pressure curves all have maxima or minima, that is, an azeotrope is formed; (ii.) it does not follow that because—

$$\frac{dP}{dx} = 0, \text{ either } \frac{dP}{dy} = 0 \text{ or } y = x.$$

On page 1799 (*loc. cit.*) Marshall's equation has been misinterpreted: x represents the composition of the liquid. As Merriman points out, x has two values (corresponding



Vapour-pressures of Ethyl Acetate and Water at 37·55°.

with the two layers) in the case considered, and neither of these is the same as y for the vapour. Marshall's equation is another way of writing $y = x$ when $\frac{dP}{dy} = 0$, and since, as has been shown above, this condition is not fulfilled, the equation is not applicable. The calculation carried out by Merriman is simply an application of Dalton's law of partial pressures.

(We are indebted to the Chemical Society for permission to reproduce the accompanying woodcut).

41. "*Direct Combination of Nitrous Acid with Primary, Secondary, and Tertiary Amines.*" By Panchanan Neogi.

Having isolated the nitrites of the primary, secondary, and tertiary amines from mixtures of their hydrochlorides and alkali nitrites (Neogi, *Proc.*, 1911, xxvii., 242; *Trans.*, 1912, ci., 1610; Chem. News, 1913, cviii., 53, 62), the author advanced the theory that an amine nitrate is formed as an intermediate compound in the interaction of nitrous acid and the amines (excepting purely aromatic amines). In continuation of the same subject, the direct action of free nitrous acid and free amine at a low temperature has been studied. It has been found that with suitable precautions pure amine nitrites are obtained by the combination of ice-cold solutions of free nitrous acid with the amines. In this way, ammonium, methylammonium, diethylammonium, trimethylammonium, benzylammonium, and piperidinium nitrites have been obtained.

42. "*The Mechanism of Nitrification.*" (Preliminary Note). By Ernest Moore Mumford.

Investigation was directed to the bacterial oxidation of aqueous solutions of ammonium salts on suitably inoculated experimental filters with a view to identify intermediate products of oxidation and determine the internal mechanism of the change.

The filters were inoculated from actively nitrifying sewage filters, the organism being checked by the customary methods.

As a result of the work, it has been found that the oxidation proceeds in a series of stages compatible with the hypothesis that bacterial oxidation is attained by successive hydroxylation of hydrogen atoms, and subsequent elimination of water.

Intermediate compounds were identified in hydroxylamine salts and salts of hyponitrous and nitrous acids, and it was found that the loss of nitrogen, which invariably takes place to a certain extent on such filters, is due in part to complex interactions between these various intermediate compounds; and, as the relative concentration of these compounds is determined by the degree of aeration of the filter, this hypothesis is in correlation with the observed difference in the loss of nitrogen between a percolating filter and a contact bed.

The hydroxylamine was identified by the sodium nitroprusside reaction, and estimated by titration with iodine solution in presence of sodium hydrogen carbonate, and the hyponitrous acid was detected by the formation of the insoluble silver salt; the nitrous and nitric acids were determined by the customary methods employed in water analysis.

43. "*α- and β-Trimethyl Cobalticyanide.*" By Ernald George Justinian Hartley.

Silver cobalticyanide and methyl iodide react at a temperature of about 45° to form silver iodide and two isomeric trimethyl cobalticyanides, together with some decomposition products. The two isomerides differ both in physical and chemical properties. One of them, which it is proposed to call the α-compound, is less soluble than its isomeride in water and the lower alcohols. It crystallises from hot water in very fine hair-like fibres somewhat resembling glass-wool.

It forms double salts with silver cobalticyanide and with silver nitrate.

The β-variety crystallises in minute needles from any of the above solvents. It also forms double salts with silver cobalticyanide and silver nitrate respectively, but of different composition from the corresponding α-compounds.

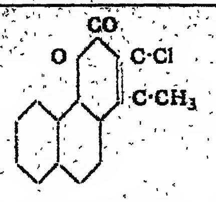
44. "*The Preparation of Dithiobenzoic Acid.*" By Gerald Noel White.

The following simple method of preparing dithiobenzoic acid, $C_6H_5{\cdot}CS_2H$, directly from benzaldehyde in one operation has been found to give satisfactory results.

A solution of 18 grms. of benzaldehyde in 300 cc. of alcohol and 150 cc. of ammonia (D 0·880) is mixed with powdered sulphur (10 grms.), and the mixture then saturated with hydrogen sulphide, first at the ordinary temperature, and finally, with frequent shaking, on the water-bath. The treatment with hydrogen sulphide is continued until all the sulphur has dissolved, and on dilution of a sample with water, no appreciable precipitate of benzaldehyde is obtained. The deep red liquid, after being diluted and shaken with benzene to remove a small quantity of unchanged aldehyde, is acidified with hydrochloric acid. The precipitate is collected and washed with ether, which is also employed to extract the dithiobenzoic acid from the acidified liquid. The substance is readily obtained as a purple oil by treating the concentrated ethereal solution with methyl alcohol.

45. "*Condensation of Ethyl α-Chloroacetoacetate with Phenols.*" By Biman Bihari Dey.

On condensing α-naphthol with ethyl α-chloroacetoacetate under suitable conditions in the presence of concentrated sulphuric acid at 0°, 3-*chloro-4-methyl-1:2-α-naphthapyrone*,—



is obtained in a 70—75 per cent yield. It crystallises from glacial acetic acid in clusters of hard colourless needles, melting at 227°. On boiling it for several hours with excess of 30 per cent alcoholic potassium hydroxide, crystals of the sodium salt of α-naphthacoumarilic acid slowly separate out, which, on acidification, is converted into the free 2-methyl α naphthafuran-1-carboxylic acid, prepared by Hantzsch and Pfeiffer (*Ber.*, 1886, xix., 1303). It melts at 248°, about 6° higher than that given by Hantzsch and Pfeiffer.

m-Cresol condenses with ethyl chloroacetoacetate to give an almost quantitative yield of 3-*chloro*-4 : 7 *dimethylcoumarin*, $C_{11}H_9O_2Cl$, crystallising from alcohol in long needles melting at 135°. On boiling with alcoholic potassium hydroxide, it is converted into 2 : 5-dimethylcoumarilic acid, melting at 218°; Fries and Fickewirth (*Annalen*, 1908, ccclxii., 51), who obtained it from the product of bromination of 4 : 7-dimethylcoumarin, gave 212° as the melting-point.

p-Cresol under similar conditions forms 3-*chloro*-4 : 6-*dimethylcoumarin*, crystallising from acetic acid in colourless needles melting at 160°; boiling alcoholic potassium hydroxide converts it into 2 : 4-dimethylcoumarilic acid prepared by Hantzsch and Lang (*Ber.*, 1886, xix., 1299).

p-4-Xylenol under the same treatment gives an 80 per cent yield of 3-*chloro*-4 : 6 : 7-*trimethylcoumarin*, $C_{12}H_{11}O_2Cl$, crystallising from alcohol in needles melting at 170°. It is converted by alcoholic potassium hydroxide into 2 : 4 : 5-*trimethylcoumarilic acid*, $C_{12}H_{12}O_3$, crystallising from ethyl acetate in colourless needles melting at 249°. On distilling the acid with excess of dry lime, the corresponding *trimethylcoumarone*, $C_{11}H_{12}O$, passes over as an oil, which solidifies on cooling in ice; it crystallises from acetone in snowy flakes melting at 39—40°.

Phloroglucinol gives a good yield of 3-*chloro*-5 : 7-*dihydroxy*-4-*methylcoumarin*, $C_{10}H_7O_4Cl$, crystallising in yellow needles melting at 308°. The *dimethyl ether*, $C_{12}H_{11}O_4Cl$, forms aggregates of short needles melting at 170°. The *diacetyl* derivative, $C_{14}H_{11}O_6Cl$, forms needles melting at 154°, and the *dibenzoyl* derivative, $C_{24}H_{15}O_6Cl$, crystallises in rhombic plates melting at 186°.

Hydroxyquinol gives a rather poor yield of 3-*chloro*-6 : 7-*dihydroxy*-4-*methylcoumarin*, $C_{10}H_7O_4Cl$, crystallising in nearly colourless needles, and melting at 259—260°. The *diacetyl* ($C_{14}H_{11}O_6Cl$) and the *dibenzoyl* ($C_{24}H_{15}O_6Cl$) derivatives melt at 172° and 192° respectively.

46. "*The Action of Phosphoric Oxide on Dibenzylmalonic Acid.*" By HUBERT CYRIL CUTTS.

As 1-hydrindone may be prepared by the intramolecular condensation of phenylpropionyl chloride (Kipping, *Trans.*, 1894, lxv., 480), it seemed probable that dibenzylmalonic acid might be converted into a compound of the constitution $C_6H_4{<}{}^{CH_2}_{CO}{>}C{<}{}^{CH_2}_{CO}{>}C_6H_4$. Attempts to bring about this change by means of phosphoric oxide resulted in the isolation of two products melting at 145° and 78° respectively. The investigation of these compounds and of their derivatives was just on the point of completion (last July) when further experiments were rendered superfluous by the publication of a paper by Leuchs, Wutke, and Gieseler (*Ber.*, 1913, xlvi., 2200). The results of these investigators, who, however, employed thionyl chloride, and the facts established by the author, showed that the compound melting at 145° was the O-dibenzylacetyl derivative of 1-hydroxy-2-benzylidene, and the compound melting at 78°, dibenzylacetic anhydride.

47. "*The Relation between the Absorption Spectra of Acids and their Salts.*" Part II. By ROBERT WRIGHT.

The examination of a number of acids and salts, with reference to their light absorbing power, seems to point to the following conclusions:—(1) The absorption spectra of strong acids are identical with those of their sodium salts; (2) moderately strong acids, such as acetic, &c., are more absorbent than their sodium salts, but the difference between the spectrum of an acid and its salt diminishes with the weaker homologues; (3) very feeble acids, such as hydrogen sulphide or arsenious acid, are less absorptive than their salts. The generalisations given do not, of course, apply to those cases where the acid and salt are of different structure.

NOTICES OF BOOKS.

The Chemistry of the Radio-elements. Part II. *The Radio-elements and the Periodic Law.* By FREDERICK SODDY, F.R.S. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1914.

THIS very important and interesting monograph deals with recent advances in our knowledge of the chemistry of the radio-elements, and their bearing upon theories of chemistry in general, and in particular upon the Periodic Law. It has been conclusively established that the method of treating the radio-elements as the analogues of known elements, with which they are chemically identical, is general, and moreover it has been proved to be generally true that an α-ray change means a shifting of the element two places to the left in the Periodic Table, while a β-ray change means the shifting of the element one place to the right. Thus a definite relation has been proved to exist between the sequence of radio-active changes and the chemical character of the products. The author has suggested the word "isotopes" "isotopic" for all elements which occupy the same place in the Periodic Table and are chemically non-separable, and the monograph contains a diagram showing the three disintegration series arranged across the Periodic Table, and the positions of the isotopic elements. The author considers that it has been abundantly proved that chemical properties alone, in the absence of any other evidence, are very insufficient criteria on which to judge the homogeneity of any material, and he regards the atomic weight of an element as a mean rather than a natural constant. The discussion of the nature of the end-products of the three series and their relation to ordinary lead is exceedingly interesting, and it is shown that chemical science has now actually discovered the way to approach the solution of the problem of the alchemist; for either the expulsion of one α-particle from thallium, or one α- and one β-particle from mercury, would give a product which would be isotopic with gold. The monograph is a highly important contribution to our knowledge of the chemistry of the radio-elements, and should be carefully studied by all who are interested in modern researches upon the structure of matter.

The Nature of Enzyme Action. By W. M. BAYLISS, M.A., D.Sc., F.R.S. Third Edition. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1914.

THE general properties of enzymes and methods of preparing and investigating them are exhaustively discussed in this book, the third edition of which has undergone extensive revision and amplification. Some chapters, for instance those on Reversibility and on the Combination between Enzyme and Substrate, and also the section on Anti-enzymes, have been almost entirely re-written, and recent discoveries in these regions are fully described. Many important additions have been made to the bibliography which is a valuable feature of the monograph.

The Observer's Handbook. Published by the Authority of the Meteorological Committee. Annual Edition. 1913.

This handbook will be found quite invaluable by those who are interested in taking meteorological observations. It contains directions for the use of all the common types of instruments, and also discusses non-instrumental observations, giving illustrations of cloud forms and tables of the Beaufort notation and international symbols. All the tables necessary for the conversion from British to Continental units and *vice versâ* are included, with specimens of returns from normal climatological stations.

Die Industrie der Cyanverbindungen. ("The Industry of the Cyanogen Compounds"). By Dr. Hippolyt Köhler. Braunschweig: Friedr. Vieweg and Sohn, 1914. (Mk. 8).

The demand for cyanogen derivatives has risen enormously in recent years, and the working up of processes for preparing them on a large scale has engaged the attention of many scientific men. This monograph gives a clear summary of the development of the industry and its present position. It is divided into three parts. The first deals with the scientific aspects of the subject, and describes in outline the chemistry of cyanogen and its derivatives. In the second part the processes employed technically for the preparation of cyanogen compounds are discussed, including methods based upon the utilisation of animal products and the products of distillation and methods in which the atmosphere is used as the source of nitrogen. The economical aspects of the different processes are considered, and statistics of cost, &c., are freely quoted. In the third section on the analysis of cyanogen compounds the methods of testing the raw material and end-products which are adapted for technical purposes are fully described.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clviii., No. 2, January 12, 1914.

Melting-point of Arsenic.—R. Goubau.—In order to determine the melting-point of arsenic the author introduced freshly sublimed arsenic into a quartz flask provided with a long narrow neck and filled with an inert gas. The closed end of a quartz tube, intended for the thermo-electric couple, was pushed down to the bottom of the flask. Round the upper half of the neck a lead coil was placed, and a rapid current of cold water was passed through it. The flask was then sunk, as far as half-way up the neck, into dry sand in a graphite crucible, and the whole was heated slowly in a Roessler gas-furnace. The arsenic vapours formed as soon as the heating began drove out the inert gas, and were condensed in the cooled neck, thus forming an effectual stopper. The thermometer rose steadily to 817°, which is apparently the melting-point of arsenic. The substance possesses a high vapour tension before this temperature is reached. If the heating is continued a violent explosion occurs at about 900°.

Two Compounds of Zirconium Chloride with Pyridine.—Ed. Chauvenet.—Matteus has already described a compound of zirconium chloride and pyridine of formula $ZrCl_4.2C_5H_5N$. Zirconium chloride is very soluble in pyridine, and on slow evaporation of the solution prismatic crystals are deposited. They have an appreciable tension of dissociation at the ordinary temperature, and often partially decompose when attempts are made to isolate them. The composition of the product generally lies between $ZrCl_4.3.5C_5H_5N$ and $ZrCl_4.4C_5H_5N$. The determination of the heat of fixation of *n* molecules of pyridine by $ZrCl_4$ (*n* lying between 2 and 4) shows that no compounds exist between $ZrCl_4.2C_5H_5N$ and $ZrCl_4.4C_5H_5N$. Water decomposes this product, setting free zirconium hydrate. The decomposition of $ZrCl_4.4C_5H_5N$, which begins at the ordinary temperature, takes place more rapidly at 50°, or *in vacuo* at 15°. The loss of weight ceases when the composition of the substance corresponds to $ZrCl_4.2C_5H_5N$.

Atti della Reale Accademia dei Lincei.
Vol. xxii. [ii.], No. 11, 1913.

Preparation of Potassium Fluomanganite.—I. Bellucci.—To prepare potassium fluomanganite finely powdered potassium permanganate is warmed in hydrofluoric acid containing potassium fluoride, and after allowing to cool sulphuric ether is added drop by drop. When all the permanganate has dissolved the whole is allowed to stand, when a copious yellow precipitate forms and may be separated by decantation. The fluomanganite may be purified by re-crystallisation from 40 per cent hydrofluoric acid.

MISCELLANEOUS.

Royal Institution.—A General Meeting of the Members of the Royal Institution was held on the 2nd inst.; Sir James Crichton Browne, Treasurer and Vice-President, in the Chair. Sir James Key Caird, Bart., Dr. Thomas W. Dewar, Prof. Frederick G. Donnan, Dr. A. Hair, Mrs. Eric Hambro, Mr. C. E. Hearson, Mr. J. Gregory Jones, Mr. J. E. Kingsbury, Captain C. Morley Knight, Dr. Vincent W. Low, Mrs. Penrose-Thackwell, and Prof. W. J. Pope were elected Members.

Compounds of Monovalent Nickel.—I. Bellucci and R. Corelli.—When nickel cyanide of formula $NiCy_4K_2$, containing divalent nickel, is reduced in alkaline aqueous solution by nascent hydrogen (using excess of potassium amalgam), a more or less intense red coloration is produced, owing to the formation of the cyanide, $NiCy_3K_2$, containing monovalent nickel. This latter is analogous to the copper salt, $CuCy_3K_2$. The red solution of $NiCy_3K_2$ is not precipitated by the addition of ammonium sulphide.—*Atti della Reale Accademia dei Lincei*, 1913, xxii., No. 10.

MEETINGS FOR THE WEEK.

Tuesday, 10th.—Royal Institution, 3. "Modern Ships," by Prof. Sir John H. Biles, D.Sc., &c.

Wednesday, 11th.—Royal Society of Arts, 8. "Bacterial Treatment of Peat, and its Application as a Fertiliser," by Prof. W. B. Bottomley.

Thursday, 12th.—Royal Institution, 3. "Heat and Cold," by Prof. C. F. Jenkin, M.A.

— Royal Society. "A Functional Equation employed by Sir George Stokes," by Sir James Stirling. "Mercury Green Line $\lambda=5461$ as resolved by Glass and Quartz Lummer Plates, and on its Zeeman Components," by J. C. McLennan and A. R. McLeod. "Electrical Condition of a Gold Surface during the Absorption of Gases, and their Catalytic Combustion," by H. Hartley. "Diffusion of Electrons through a Slit," by J. H. Mackie. "Rate of Solution of Hydrogen by Palladium," by A. Holt.

Friday, 13th.—Royal Institution, 9. "An Indian State," by Sir Walter R. Lawrence, Bart.

— Alchemical Society, 8.15. (At International Club, Regent Street, S.W.). "Roger Bacon," by B. R. Rowbottom.

— Physical, 8. "Time Measurements of Magnetic Disturbances and their Interpretation," by C. Chree. "Ratio of the Specific Heats of Air, Hydrogen, Carbon Dioxide, and Nitrous Oxide," by H. N. Mercer. "Asymmetric Distribution of the Secondary Electronic Radiation produced by X-Radiation," by A. J. Philpot.

Saturday, 14th.—Royal Institution, 3. "Recent Discoveries in Physical Science," by Prof. Sir J. J. Thomson, O.M., F.R.S.

THE CHEMICAL NEWS.

VOL. CIX., No. 2833.

MAGNETIC SUSCEPTIBILITIES OF THE ELEMENTS.

By F. H. LORING.

THE magnetic susceptibilities of the pure elements are of scientific interest, and since these are rarely given in a collected form, except in compiled tables of physical and chemical constants, it may be of some interest to study these properties by suitably arranged tables. An attempt is here made to present the data in an orderly and possibly instructive form. A brief mention of the magnetic principles involved will be given first.

The familiar expression,—

$$\mu = B/H \quad . \quad . \quad . \quad . \quad . \quad (1),$$

signifies that the permeability μ is a *ratio* derived from the number of magnetic lines of force, B, per unit cross-sectional area in the iron, for example (say, per square centimetre), divided by H, the number of magnetic lines of force that would be developed in the same unit area of air, or empty space, the magnetising force being the same in each case. That is to say, a coil carrying a given current (or, to be more precise, of given ampère turns) will produce more magnetic lines of force in the iron within it than in the air or empty space when the iron is removed, and this ratio, whatever it may happen to be, is termed the *permeability*. Of course, tests in proof of this relation have been made under *suitable conditions* which need not be detailed here.

The permeability varies with the quality, state, history, &c., of the iron, as to whether it is soft, hard, &c. The magnetising force, H, coincides with the magnetic lines producible in the air or empty space, and these descriptive terms are exchangeable, as space or air free from magnetic substance has no varying permeability or multiplying power, being taken as *unity*. In other words, the number of magnetic lines of force in free space or air numerically represents the magnetising force. (The expression "magnetic lines of force" is supposed by some to have a physical meaning, as if the magnetism actually extended in thread-like lines. On the other hand, others regard this term as too descriptive, and they say that it should only be accepted as conventional, and that no such *line* conception should be entertained. However, the picturesque term is preferable, but the possibility, or even probability, that it is merely a conventional device should be kept in mind. It is true that this conception implies *direction* and the number of lines indicate *strength*, so that the expression is quite in order).

From the following Table (I.) these variables may be noted. This table is copied from "C. G. S. System of Units," 1891, p. 148, by J. D. Everett, the figures being based upon the measurements of Ewing and Bidwell on iron, which may be taken as fairly characteristic.

In this table the term k is given, which is the *magnetic susceptibility*. Iron, cobalt, and nickel have a high susceptibility which passes through a wide range of magnitude as compared with all other elements* (see Table II.), k being particularly variable in highly magnetic (ferromagnetic) metals, such as iron. The susceptibility is also a ratio, like the permeability, being the ratio of the intensity of the *induced* magnetism (I) to the magnetising force (H); the relation may be expressed thus—

$$I/H = k \quad . \quad . \quad . \quad . \quad . \quad . \quad (2).$$

* There are some rare elements which have not been thoroughly investigated in the pure state (see below).

TABLE I.

H. Magnetising force.	I. Magnetisation.	k. Susceptibility.	B. Induction.	μ. Permeability.
0·3	3	10	41	128
1·4	32	23	413	299
2·2	117	53	1460	670
3·5	574	164	7230	2070
4·9	917	187	11540	2350
6·7	1078	161	13520	2020
10·2	1173	115	14840	1450
22·3	1249	56	15710	705
78·0	1337	17	16900	215
208·0	1452	7	18500	89
585·0	1530	2·6	19800	34
24500·0	1660	0·067	45300	1·9

The term I at first glance seems unnecessary, as it is already seen that the magnetising force (H) gives rise to so many lines per square cm. (B) in the metal or substance, according to its permeability (μ). By a somewhat artificial procedure, the induction B may, however, be divided into two components, *one* being the magnetic lines of force due to the magnetising force H, as produced in empty space or air, and the *other* due to the magnetic lines of force which are *induced*, or called into existence, or influenced, so to speak, by the peculiarity of the substance acted upon by the magnetising force; whether, for example, it be *paramagnetic* like iron, or *diamagnetic* like bismuth; therefore, calling the intensity of magnetisation due to, or induced through, the agency of the substance, I, and the lines of magnetic force that would be produced in air or empty space H, which becomes the magnetising force, the following equation represents the union of these two factors:—

$$B = 4\pi I + H \quad . \quad . \quad . \quad . \quad . \quad (3).$$

(This equation is truly *algebraic*, since it holds good if the signs change; see below. The 4π term, or multiplier, arises from the old conception of 4π lines emanating from a sphere of unit radius (= unit pole), and appears in these calculations of the magnetic circuit).

It is therefore apparent that if the substances exercise variable positive and negative modifying influences, the magnetic susceptibility of any particular substance may be defined by the ratio of H to I, as shown by Equation 2, and this ratio, moreover, may be positive or negative, according to the inherent nature or characteristic of the material (see Tables II. and III.)

Having established the fundamental relations, it is obvious that different formulæ may be constructed thus:—

It was shown that—

$$B = 4\pi I + H,$$

and by definition of k,—

$$I = kH;$$

hence—

$$B = 4\pi kH + H = (4\pi k + 1)H,$$

whilst—

$$B = \mu H;$$

therefore—

$$\mu = 4\pi k + 1$$

and—

$$k = \frac{\mu - 1}{4\pi},$$

which are all well-known expressions (see Ewing, "Magnetic Induction in Iron and other Metals," 3rd Edition, 1910, pp. 12 and 18).

While the permeability of air is taken as 1, and its susceptibility as zero, when studying the permeability and susceptibility of highly magnetic substances such as iron, cobalt, &c., *air*, as a matter of fact, is very feebly magnetic, and for an absolute comparison (or correction) a vacuum may be taken, which is absolute unity in one case and absolute zero in the other. The following values by volume ($k_v \times 10^6$) may be of interest in this connection:—

TABLE II.—*Paramagnetic Elements.*

	Positive susceptibilities for unit mass, given in $10^6 \times k_m$ values; k_m being the susceptibility, which may be calculated by multiplying these values by 10^{-6}.	Corresponding values for unit volume, $10^6 \times k_v$.
Fe	+31,170,000 (*a*) wrought iron.	
Co	+1,842,000 (*b*) cast cobalt.	
Ni	+2,003,000 (*c*) annealed nickel rod.	
O_2	+436 at −259° (solid)	+324 at −182°
Mn	+20 „ 1000° (+11 at 18°)	
Pd	+5·8 „ 18° (+2 at 1100°)	+50 to +60
Cr	+4·2 „ 1100° (+3·7 at 18°)	
Ti	+3·5 „ 1100° (+3·1 at 18°)	
Rh	+1·9 „ 1150° (+1·1 at 18°)	+13
V	+1·8 „ 1100° (+1·5 at 18°)	
Nb	+1·3 „ 18°	
Pt	+1·1 „ 18° (+0·7 at 1000°)	+23 to +29
Ta	+0·93 „ 18° (+0·8 at 800°)	
Be	+0·79 „ 15°	
Al	+0·65 „ 18° (+0·5 at 1000°)	+1·7 to +1·9
Mg (cryst.)	+0·57 „ 20° (+0·55 at 18°)	
Na	+0·51 „ 18°	
K	+0·40 „ 18—180°	
Li	+0·38	
W	+0·33 „ 18—1100°	
Ir	+0·3 „ 1100° (+0·15 at 18°)	+4·9
Th	+0·3 „ 400° (+0·18 at 18°)	
Os	+0·04 „ 18—1100°	
Mo	+0·04 „ 18°	
Sn	+0·03 „ 18—240°	+0·35
Si (see Table III.)	+0·01 „ 16° (cryst.) (St. Meyer)	
N_2 (atmospheric pressure)		+0·001 at 16°

Explanatory Note.—The second column gives the values ($10^6 \times k_m$) for elementary substances of the first column (not single atoms). Values marked *a*, *b*, *c* are fairly characteristic, and show the enormously greater susceptibilities of these elementary substances under conditions of practically the highest susceptibility. The bracketed values show lower values for the temperatures (°C.) specified.

TABLE III.—*Diamagnetic Elements.*

	Negative susceptibilities for unit mass, given in $10^6 \times k_m$ values; k_m being the susceptibility, which can be calculated by multiplying these values by 10^{-6}.	Corresponding values for unit volume, $10^6 \times k_v$. A = atmospheric pressure.
He		−0·002 at 0° (A)
H_2		+0·008* at 16° (A); −0·005† at 15° (A)
Ar		−0·10 at 0° (A)
Cu	−0·09 at 18—1000°	−0·66 to −0·80
Si (cryst.)	−0·12 „ 18° (Honda). (See Table II.)	
Pb	−0·12 „ 18—330°	−1·4 to −0·84
Zn	−0·15 „ 18 (−0·10 at 650°)	−0·70 to −1·0
Au	−0·15 „ 18—1060°	−3·1
Cd	−0·17 „ 18° (−0·15 at 700°)	
Hg	−0·19 „ 18—250°	−2·6 at 19°
Ag	−0·22 „ 1100° (−0·19 at 18°)	−1·7 at 15°
As	−0·3 „ 18—200°	
Se	−0·32 „ 18°	−0·50 (red selenium) (−1·3 melted)
Te	−0·32 „ 18—440°	−2·1 and −1·6 (−0·6 at 18°)
I (cryst.)	−0·35 „ 18°	
Br	−0·38 „ 18°	−1·4 at 19°
Zr	−0·45 „ 18° (−0·3 at 1150°)	
S	−0·48 „ 18—300°	−0·77 to −0·9
C (diamond)	−0·49 „ 18—500°	
Cl_2	−0·59 „ 16° (A)	
B	−0·8 „ 1100° (−0·71 at 18°)	
P (white)	−0·88 „ 18°	−1·6 at melting-point
Sb	−0·94 „ 18°	−5·6 to −3·8
Bi	−1·4 „ 18° (−0·04 at 273—405°)	−16 at −182° (−14 at 15°)
C (arc carbon)	−2·0 „ 18° (−1·5 at 1150°)	
C (graphite)		−8 at 18°

* Quincke. † Bernstein.

In general, the Explanatory Note below Table II. applies to this table. In both tables, where no temperatures are given, it may be assumed that no appreciable variation from laboratory temperatures occurred. The unbracketed values, as in Table II., are principally the highest ones given in the Landolt-Börnstein compilation.

H_2 at atmos. pressure	=	-0.005,	at 40 atmos.	=	0.000
N_2	"	" =	$+0.001$,	" " =	$+0.04$
O_2	"	" =	$+0.129$,	" " =	$+6.2$
Air	"	" =	$+0.032$,	" " =	$+1.3$

Temperature in each case except first one, 16° C. (see Table III.). Water at 20° C. = -0.75.

Referring to Table III., it will be seen that no element has been discovered which has a negative susceptibility sufficiently high to make the permeability ($4\pi k+1$) negative. A *paramagnetic* substance has a permeability greater than 1, and a positive susceptibility. A *diamagnetic* substance has a permeability less than unity or empty space, and a negative susceptibility. No known substance is more than slightly diamagnetic, bismuth having a negative volume susceptibility of -16×10^{-6}, and a corresponding permeability only slightly below 1, namely, 0·9998.

Tables II. and III. are self-explanatory. The values, except *a*, *b*, and *c*, are taken from the "Landolt-Börnstein Physical Tables," 1912, p. 1241. While a selection in each case of practically the highest value given in the Landolt-Börnstein table is made, higher values are possible in some cases under chosen conditions of maximum susceptibility. Practically all the mass values of the weakly magnetic elements are those by Honda, the field strength being 10·5 kilogauss. The usual ferromagnetic measurements are by *volume*, but since the specific gravity of a substance is the weight of a unit volume of the substance compared, the susceptibilities may be converted into mass values by dividing the volume values k_v by the density of the element $=k_m$. The suffixes are not always used, as it is understood from the context which magnitude is intended. The volume values in the tables may not be exactly convertible into the mass values given, as the figures relate to distinct experiments often conducted by different experimenters.

Recent work by K. Ihde (*Ann. Physik.*, 1913, xli., 829—853) points to higher values for manganese and chromium than shown in Table II., especially under altered physical conditions, the former element having a susceptibility $k=88.3\times10^{-6}$, the field strength being 1000 lines per square centimetre. At a lower field strength a higher value is probable. Powdered manganese subjected to a field of double this strength gave $k=66.5\times10^{-6}$ (coarsest powder) to 156×10^{-6} (finest powder). Chromium in a compact or massive state with a field strength of 1000 lines per square centimetre gave $k=39.3\times10^{-6}$, and in a powdered state with a field strength two times greater gave $k=33.4$ to 65.4×10^{-6} for coarse and fine powders respectively.

(To be continued).

CONSTITUTION OF HYDRATES.

(PART I.).

By JAMES MACLEOD-BROWN.

MANY papers on the behaviour and properties of salts containing water of hydration have appeared in various journals, but no explanation of the way in which the water is combined in the molecule has yet, so far as the author is aware, been generally accepted. The following theory, depending on the variability of valence, seems to be consistent with the facts:—

Cupric sulphate is usually taken to illustrate the different hydrates which a salt may form. It forms three hydrates, viz., the mono-, tri-, and pentahydrates:—

$$CuSO_4 \rightleftharpoons CuSO_4.H_2O \rightleftharpoons CuSO_4.3H_2O \rightleftharpoons CuSO_4.5H_2O.$$

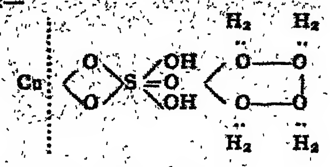
The water in the monohydrate is strikingly different from the other four molecules of water, inasmuch as it is set free at a temperature of not much below 200°. This fact tends to show that this molecule of H_2O is an entirely different function from the other four.

Of the remaining four molecules they are combined in two different ways; *i.e.*, two of the molecules of water are combined similarly; the other two are also combined similarly, but in such a manner that they are more strongly attached than the other two. If these four molecules were all combined in the same manner the formation of $CuSO_4.3H_2O$ would doubtless be impossible, for all the four molecules would be liberated together, thus:—

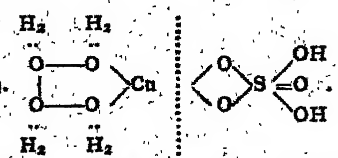
$$CuSO_4 \rightleftharpoons CuSO_4.H_2O \rightleftharpoons CuSO_4.5H_2O;$$

or else they could be set free individually, and a series of hydrates containing five, four, three, two, and one molecules of water respectively would be formed. As hydrates of $CuSO_4$ containing two or four molecules of water are unknown, the molecules must be connected as explained above.

Two constitutional formulæ have been suggested by the writer, viz.:—

(1). 

and—

(2). 

The dotted line in each case dividing anion from cation.

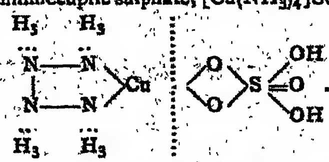
In (1) the anion is extremely complex. There are other objections to this formula which will be gone into more thoroughly in a future communication.

Formula (2) shows the anion and cation more evenly balanced. It might be objected to on the grounds that the existence of tetravalent copper is somewhat doubtful. The writer does not think this objection can hold, because the greater number of the elements are known to form compounds in which their valency varies by multiples of two. Some elements form compounds in which their valency differs by only one.

If the second formula illustrates the constitution of cupric sulphate pentahydrate we should be able to obtain compounds possessing the constitution—

$$[CuWx.Ry]SO_4.H_2O,$$

where Wx represents number of molecules of unsubstituted OH_2 groups, Ry the number of groups substituted by R, and $x+y=4$. Compounds of this constitution may be readily prepared in the laboratory; the best known is probably tetramminecupric sulphate, $[Cu(NH_3)_4]SO_4.H_2O$, or—



Part II. of this article will deal with the chemical behaviour of hydrates, viewed from the standpoint of the theory outlined above.

11, Kent Gardens, Ealing, London, W.

Literary Intelligence.—Messrs. J. and A. Churchill have much pleasure in announcing the two following new works:—"Molecular Physics," by J. A. Crowther, M.A., Demonstrator in Physics, Cavendish Laboratory, Cambridge; with 29 illustrations. "The Synthetic Use of the Metals in Organic Chemistry," by A. J. Hale, B.Sc., Demonstrator, City and Guilds of London Institute, Technical College, Finsbury.

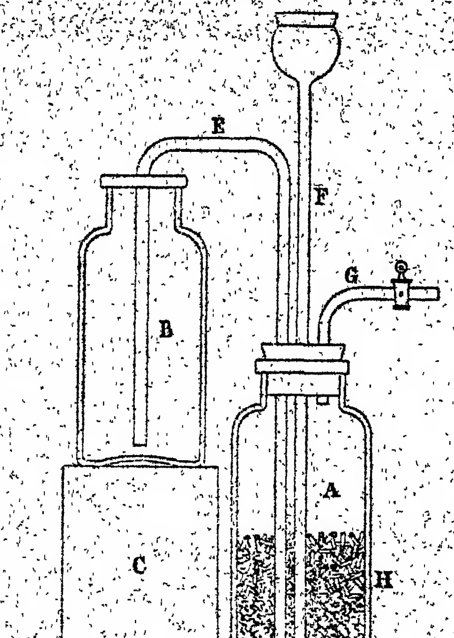
AUTOMATIC GAS GENERATOR.

By ROBERT W. CURTIS.

The form of generator shown in the cut may be put together in a few minutes from ordinary materials at hand in any laboratory, and has a number of advantages, as will appear.

A small size may be made up as follows:—The bottle A is a 16 oz. salt mouth, B 12 oz., and the block C 4$\frac{3}{4}$ in. high. The tubes E and F must fit the stopper so as to be gas tight and yet allow sliding the stopper. Size No. 4 glass tubing may be used for E in order to permit easy passage of liquid through it. The outlet G is provided with a glass stopcock, or a pinchcock could be used on the rubber connection.

In charging the apparatus the stopper is pushed up on the tubes E and F, which are held in place while pieces of broken chemically resistant material (*e.g.*, firebrick) is dropped in A to the level of H, evenly distributed by shaking. Upon this is put a layer of the material for generating the gas. The stopper is then pushed down into



place, the outlet opened, and dilute acid or other reagent, sufficient to rise above H, is added through F. When the stopcock is closed the syphon E becomes operative, and the apparatus is thereafter auomatic.

A difficulty with many automatic generators is their "running down" by continuous slight action when not in use, as over night, due to a small leakage of gas. This is effectually prevented by lifting the bottle A, thus removing E from dipping in the liquid in B, and placing A where any drip from E may fall into a sink or beaker. To start up it is only necessary to replace A, and introduce enough of the liquid through F to fill E.

If the syphon is "lost" at any time it is but the matter of a moment to re-fill E similarly. If the admission thus of a little air into the gas is objectionable, a separatory funnel may be used instead of F.

The reagent in passing back and forth through E is thoroughly mixed with the spent liquor. Fresh reagent may be added at any time through F or in B, and waste removed easily from B. The whole apparatus can be thoroughly rinsed out through F and E without disturbing any adjustments. There is no possibility of leakage of the liquid reagent. The arrangement is so simple, portable, and easily set up that a number may be constructed as needed.

If a three-necked Woulfe bottle were substituted for A the central neck could be closed by the stopper carrying the outlet G. The removal of this stopper would render easier the replenishing of the solid reagent.

The dimensions could be varied to meet different requirements; as increasing the height of C to obtain greater pressure, or the size of A to give greater reservoir capacity, or the diameter of B to increase the supply of liquid reagent without much increase of pressure.

College of the City of New York,
Feb. 12, 1914.

THE SCIENTIFIC WEEK.

(*From Our Own Paris Correspondent*).

The Mineralogical Constitution of the Shetland Isles.

M. E. Gourdon, geologist of the French Antarctic Exhibition (the Charcot Mission), has studied the geological constitution of the Shetland Islands. Deception Isle affects the curious form of an almost perfect ring of land; the narrow passage by which the little inland sea communicates with the ocean measures barely 200 metres of navigable width. It is an immense crater invaded by the sea. In the island that is entirely volcanic, the glacier phenomenon is to be found side by side with the volcanic phenomenon; fumaroles of 90° are to be found even in the midst of fields of snow; layers of ice alternate with the layers of ashes. The island is formed of yellow tufas, in the midst of which crop out oozings formed by trachytes, ondesites, and labradorites. Large blocks of basalt are also to be met with.

The Mammoth of the Museum.

The mammoth found four years ago in the Liakowsky Islands in the extreme north of Siberia, and offered by the Count of Stenbock Fermor to the Paris Natural History Museum, has just been naturalised. Its state of preservation is absolutely remarkable. M. Edmond Perrier, director of the Museum, has informed the Academy of Sciences concerning the histological studies undertaken by M. Gautrelet about this proboscidian that lived several centuries ago. The muscular fibres are atrophiated, but the conjunctive frame still subsists. M. Gautrelet has been able to discover, in the interior of the veins, blood that has naturally undergone great modifications, but it has kept its essential elements.

Pure Metals.

A very important progress in the preparation of refractory metals of very great pureness has just been made in the laboratories of the Institute of Applied Chemistry. Prof. Albin Haller has, in fact, presented a paper of a young and clever chemist, M. Maurice Billy, who has found a very interesting general method. This method is very simple. Up till now refractory metals were prepared by reducing their chlorides by hydrogen or by sodium. The high temperature required when hydrogen is employed, and the great difficulty of employing sodium without oxidation, have always been the cause of the impurities introduced into the metal. Thus, to prepare the most refractory metal, titanium, the method adopted was that of Petterson and Nilsen, which consists in heating to a dark red, liquid chloride of titanium in presence of sodium in a steel bomb screwed down tight. The reaction is extremely violent; the metal is almost pure, but contains traces of iron. In view of obtaining metals perfectly free from iron, silicium, and oxygen, M. Maurice Billy has made hydride

of sodium react on chloride of titanium or of vanadium at about 400°. All the inconveniences of high temperatures and violent reactions are avoided. The operations can be made in apparatus of fusible glass, and the reaction takes place in a vessel of melted sea-salt. The quantities vary according to the way the operation is performed. M. Blily has obtained as much as 50 per cent of rigorously pure metal, compared with the quantity of sodium employed. The pureness obtained is such that the titanium does not contain 1/10,000th of a mgrm. of iron. Prof. Haller remarks that it may already be considered that the reduction of metallic chlorides by hydride of sodium constitutes a general method for the preparation of pure metals, such as physico-chemistry requires to-day.

THE LONGEST TELEPHONIC CIRCUIT OF THE WORLD.

The longest European telephone lines do not exceed 1400 to 1500 kilometres. The telephonic circuit of Paris-Rome is only 1500 kilometres long and that of Paris-Vienna only 1450 kilometres. In America the length of 3200 kilometres has been attained with pupinised wires of 4 millimetres in diameter. The electric transmission can only be obtained with difficulty over greater distances. The two stumbling blocks to be avoided in telephony at a distance are the alteration of the voice caused by the distortion or deformation of the waves of sound on the one hand and the weakening of the sound produced by the diminution of the amplitude of the waves produced on the other. A distinguished engineer, M. Drumaux, has just studied the conditions of a good transmission. In order to have an excellent result it would be necessary to space the spools of Pupin, inserted in the circuit from the twelfth or fourteenth of the wave-length; that is to say, about 10 kilometres. An American company proposes, by utilising the latest improvements of the telephonic industry, to unite New York by telephone with Los Angeles and San Francisco. The distance to be covered is about 5600 kilometres. The circuit will be constituted with copper wires of 4½ millimetres in diameter, and supplied with Pupin's coils or spools, which which will be placed at intervals of 14 kilometres. As on account of the difference of time between New York and San Francisco the circuit will be utilised only for a short time, the price will be fixed at a relatively high rate for the exchange of communications. These rates will reach prices unknown in Europe, and in all probability will vary from 80 to 100 francs for three minutes' conversation.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, February 26, 1914.

SIR WILLIAM CROOKES, O.M., President, in the Chair.

Papers were read as follows:—

"*Diffraction of Light by Spheres of Small Relative Index.*" By Lord RAYLEIGH, O.M., F.R.S.

"*Studies of the Processes Operative in Solutions XXXI. Sulphonic Acids and Sulphuric Acid as Hydrolytic Agents: a Discussion of the Constitution of Sulphuric and other Polybasic Acids, and of the Nature of Acids. XXXII. The Influence of Sulphonates on the Hydrolytic Activity of Sulphonic Acids: a Contribution to the Discussion on the Influence of Neutral Salts.*" By Prof. H. E. ARMSTRONG, F.R.S., and Prof. F. P. WORLEY.

"*Morphological Studies of Benzene Derivatives. V. The Correlation of Crystalline Form with Molecular Structure: a Verification of the Barlow-Pope Conception of 'Valency-volume.'*" By Prof. H. E. ARMSTRONG, F.R.S., R. T. COLGATE, B.Sc., and E. H. RODD, B.Sc.

"*Magnetic Properties of Iron when Shielded from the Earth's Magnetism.*" By Prof. ERNEST WILSON.

When iron is subjected to a considerable magnetising force, a species of polarisation is produced which has the effect of reducing the permeability and increasing the dissipation of energy due to magnetic hysteresis for given values of the magnetic induction. The residual effects can be removed by careful demagnetisation or annealing. It was thought by analogy that the earth's magnetic force would also have a polarising influence upon exposed iron, and this is the subject of the present paper. An effort has been made to remove the residual effects of the earth's magnetism by placing the specimen, which is of ring form, in a magnetic shield, and carefully demagnetising it. The magnetic properties of the material were then examined in the usual manner with a ballistic galvanometer, and a comparison made with those obtained from the exposed or unshielded specimen. It has been found that the permeability of *freshly* demagnetised and shielded iron, corresponding to a given value of the magnetic induction, is considerably larger than in the case of the unshielded specimen. In Stallery the ratio of the permeabilities has a maximum of 1·79 when the magnetic induction is 172. The permeability rises to a maximum of 5900, and one would anticipate a considerably larger initial permeability than is generally supposed. The permeability has been examined after varying periods of rest when the specimen is in a carefully demagnetised condition, and it is shown that its values gradually decrease as the duration of rest increases. Further experiments are contemplated to discover if this diminution is due to imperfect shielding, or if the iron, when perfectly shielded, would diminish its permeability by intermolecular action. The dissipation of energy due to magnetic hysteresis is examined when the magnetic induction has values as low as 0·68. It is found that the shape of the loops suffers a marked change, becoming parallel straight lines when the smallest magnetising forces are employed. It is well known that the Steinmetz Index tends to increase as the lower forces are approached. The experiments indicate that the Index tends to again diminish both in shielded and unshielded iron.

"*Occurrence of Ozone in the Upper Atmosphere.*" By J. N. PRING, D.Sc.

This investigation was concerned with the estimation of ozone in the atmosphere at altitudes ranging up to 20 kilometres, and the distinction of this gas from other substances, such as the peroxides of hydrogen and nitrogen, which show very similar chemical reactions. A method was devised which enabled these measurement to be made under conditions which prevail in the atmosphere.

The chemical reagent used for this purpose enabled approximately quantitative results to be obtained when used in light apparatus which were attached to free balloons, and gave the following results:—

That in the Alps, at an altitude of 2100 metres, the mean concentration of ozone is about 2·5 parts by volume in 1 million of air, and at an altitude of 3600 metres about 5 parts in one million of air.

In this country the *mean* quantity found between ground-level and an altitude of 20 kilometres was about 2 parts by volume in 1 million. No trace of either hydrogen peroxide or nitrogen peroxide could be detected in these cases.

Measurements made in the laboratory on the action of ultra-violet light on air showed that a definite equilibrium amount of ozone is obtained, and that this value increases with fall in temperature, but decreases rapidly with fall in pressure.

The formation of hydrogen peroxide or nitrogen peroxide by ultra-violet light radiation could not be detected.

"*A Meteoric Iron from Winburg, Orange Free State.*" By W. A. D. RUDGE.

In this paper some account is given of the structure, and mechanical and magnetic properties of the Winburg

meteorite, which is stated to have fallen in 1881. It appears to be composed of large crystals of ferrite with veins and crystals of an iron nickel alloy. The total amount of nickel is not more than 3 per cent. Flakes of the alloy can readily be separated from the ferrite, owing to its insolubility in dilute acid. Very fine crystals of alloy are found enclosed in the ferrite crystals. The material will stand a stress of nearly 10 tons per square inch before yielding occurs, and in the elastic limit Young's modulus is nearly the same as that for pure irons. By submitting a piece of the metal to a pressure of 7000 lbs. dead load, "slip" bands were developed, which showed evidence of twinning having been set up. The magnetic properties are very similar to those of Swedish iron, but for moderate field strengths the susceptibility is decidedly greater, and for very strong fields somewhat less.

"*Electrification produced during the Raising of a Cloud of Dust.*" By W. A. D. Rudge.

During the raising of a cloud of dust a considerable amount of electrification occurs. Insulated conductors held in a stream of dust become charged to a potential of some hundreds of volts. The dust particles seem to be charged by friction amongst themselves, some with positive, others with negative, electricity. If a cloud is raised by blowing air through a wash-bottle containing finely divided material, the air accompanying the cloud becomes strongly charged, and this charge persists in the air for some time. The sign of the charge carried by the air depends upon the nature of the material. Mercury sulphide, sand, molybdic acid, and "acidic" bodies in general give negative electricity, whilst coal, flour, red-lead, alkaloids, and "basic" bodies give positive electricity. A very small amount of dust, 10^{-10} grms. per cc. will give rise to quite strong charges. The finer the material the stronger and more persistent is the charge.

"*Electrical Ignition of Gaseous Mixtures.*" By Prof. W. M. Thornton.

This is an experimental examination of the mechanism of ignition of gaseous mixtures by electrical sparks. It is found that there are two distinct types of curves connecting percentage of gas in air, and the least current which, when broken, causes ignition by the break-spark. In one, characteristic of continuous currents, the current required is proportional to the percentage of gas present; in the other, of alternating current type, it is a quadratic function of the percentage, having a minimum, at the mixture giving combustion, midway between CO and CO_2. In the paraffin series the minimum continuous current is the same for all the gases, but with alternating current the gases with more complex molecules require larger igniting currents. The slope of the one type and the minimum current of the other are both proportional to the number of atoms in a molecule of combustible gas, more nearly to the hydrogen atoms. It is inferred from the observations that ignition by continuous current break-sparks is largely ionic or electronic, but that that by alternating currents is more nearly a simple thermal process. The gases examined were hydrogen, carbon disulphide, benzene, alcohol, and the paraffin series up to pentane.

CHEMICAL SOCIETY.

Ordinary Meeting, February 19, 1914.

Prof. W. H. Perkin, LL.D., F.R.S., President, in the Chair.

The President referred to the loss sustained by the Society through the death of Gustavus Anthony Abrines (Gibraltar), Charles Cunningham Connor (Belfast), and Arthur Ellson Davies (Edinburgh).

Certificates were read for the first time in favour of Messrs. Arthur Baxter, B.Sc., 360, York Road, Camden Road, N.; Albert Coulthard, B.Sc., Ph.D., 9, Portland Avenue, Stamford Hill, N.; Robinson Percy Foulds, M.Sc., Stanley Villa, Colne; Arthur Bertram Hobson, M.Sc., 13, Westy Lane, Latchford, Warrington; James Riddick Partington, B.Sc., The University, Manchester; Walter Ryley Pratt, B.Sc., 17, Bloomsbury Square, W.C.; Walter William Reeve, B.Sc., 4, Gowlett Road, East Dulwich, S.E.; Herbert Corner Reynard, B.Sc., West Ewell, Epsom.

Certificates have been authorised by the Council for presentation to ballot under By-law I. (3) in favour of Messrs. Clifford Girdlestone Gill, Cawnpore Sugar Works, Ltd., Cawnpore, India; Yusuf Ismail Mulla, Alembic Laboratory, Club Road, Mandalay Shore, Burma.

The President announced that the following changes in the Offices and Council were proposed by the Council:—

Vice-Presidents to Retire—Dr. G. T. Beilby and Prof. W. Jackson Pope.

Ordinary Members of Council to Retire—Sir Boverton Redwood, Bart., Mr. W. R. Bousfield, Prof. H. Marshall (deceased), Prof. F. G. Donnan.

As *President*—Prof. W. H. Perkin.

As *Vice-Presidents who have filled the Office of President*—Prof. H. E. Armstrong, Prof. A. Crum Brown, Sir William Crookes, Sir James Dewar, Prof. H. B. Dixon, Prof. Percy F. Frankland, Dr. A. G. Vernon Harcourt, Prof. R. Meldola, Dr. H. Müller, Prof. W. Odling, Sir William Ramsay, Prof. J. Emerson Reynolds, the Right Hon. Sir Henry E. Roscoe, Sir Edward Thorpe, and Sir William A. Tilden.

As *Treasurer*—Dr. Alexander Scott.

As *Hon. Secretaries*—Dr. Samuel Smiles and Prof. J. C. Philip.

As *Foreign Secretary*—Prof. Arthur W. Crossley.

As *Vice-Presidents*—Prof. H. Brereton Baker, Prof. P. P. Bedson, Dr. Horace T. Brown, Mr. C. T. Heycock, Prof. E. J. Mills, and Prof. G. T. Morgan.

As *New Ordinary Members of Council*—The Earl of Berkeley, Dr. R. H. A. Plimmer, Dr. G. Senter, Prof. J. M. Thomson.

Dr. Samuel Rideal, Prof. J. J. Dobbie, and Sir Alexander Pedler were elected Auditors to audit the Society's Accounts.

Messrs. G. Fowles and H. Rogerson were elected Scrutators, and a ballot for the election of Fellows was held. The following were subsequently declared duly elected:—Ethelbert William Blair, B.Sc.; Albert Frederick Calvert; Sydney George Clifford; Lionel Cohen; Behari Lál Dás; Sydney Edward Davenport; Thomas Alexander Davidson; Thomas Eynon Davies, B.Sc.; Richard Charles Denington; Charles George Fernie, B.Sc.; George Ingle Finch; Reginald Furness, M.Sc.; John Garth; Ivan Richard Gibbs, B.A.; James Stanley Hale; Theophilus Harper; Eric Russell Harrap; Oswald Ryle Horwood, M.A., M.R.C.S., L.R.C.P.; Manappadam Ramaswami, Viswanatha Iyer; Dan Ivor James, M.A., B.Sc.; Gopal Balkrishn Kolhatker, M.A.; Alfred John Leigh, B.Sc.; Frederic William Leighton; Alex. Williamson McLaren; Archibald Macpherson; Fredk. Arthur Makin; Thomas Morris; Raymond William Nichols; William Julian Odlum, B.A.; Rowland Ernest Oldroyd; Frederick Alfred Pickworth; William Henry Pick, B.Sc.; Conley Hunter Riley; William Pawson Robson, B.A., Ph.D.; Chandra Bhusan Roy, M.A.; Joseph de Carle Smith (junior), B.Sc.; Charles Alfred Stamp; Horace Gilbert Stone, B.Sc.; Harold Edwin Temple; Eustace Ebenezer Turner, B.Sc.; Robert James Wright, M.A.

Of the following papers those marked * were read:—

*48. "*The Production of High Vacua by Means of Finely Divided Copper.*" By Thomas Ralph Merton.

It has been found that the vapour pressures of gases absorbed by finely divided copper are so low that the absorption of gases by this substance may be used for the production of high vacua.

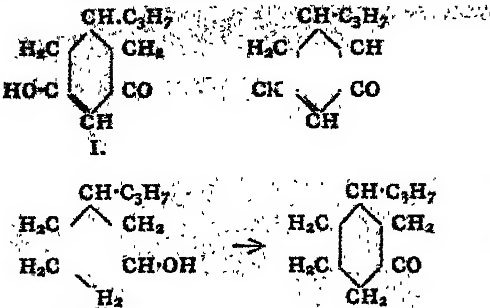
DISCUSSION.

Prof. H. B. BAKER was able to confirm Mr. Merton's results, as, in some work he had done with Prof. Strutt, a tube of copper gauze which had been left with a pressure of 1—2 mm. of nitrogen over night was found next morning to resist the passage of a very powerful electric discharge. He thought that the method would be of great importance in dealing with small traces of gases.

Dr. LOWRY suggested that the power of absorbing gases was perhaps a function of the amorphous, as contrasted with the crystalline, form of copper. This was in agreement with the fact that this power was lost on heating to 250°, a temperature that was practically identical with the annealing-temperature of hard-drawn copper wire; further, that repeated heating at lower temperatures produces the same effect.

*49. "*Hydroaromatic Ketones.* Part III. 1-iso*Propyl*cyclo*hexan*-3-*one*." By ARTHUR WILLIAM CROSSLEY and WALTER RYLEY PRATT.

1-iso*Propyl*cyclo*hexan*-3-*one* (II.) has been prepared from 1-*iso*propyldihydroresorcin (I.) by a series of reactions indicated by the following formulæ:—



I. III. II.

It boils at 208°, gives a *semicarbazone* melting at 187°, and a liquid *oxime*, the *benzoyl* derivative of which melts at 91—92°.

1-iso*Propyl*cyclo*hexan*-3-*ol* (III.) is a viscid liquid, boiling at 114°/28 mm., and possessing a characteristic pungent odour. The o-*nitrobenzoyl* derivative crystallises in small white prisms, melting at 47—48°. Both the alcohol and the ketone give β-*iso*propyladipic acid on oxidation with potassium permanganate.

It is intended to make the ketone the starting-point in the synthesis of certain meta-terpene derivatives, as it has been found possible by varying the original conditions (*Trans.*, 1902, lxxxi., 676) to improve the yield of *iso*propyldihydroresorcin so that it may now be obtained in about 70 per cent of the theoretical amount.

*50. "*The Spitting of Silver.*" By HERBERT BRERETON BAKER.

The amount of oxygen absorbed by melted silver is so large that it seems difficult to explain on the hypothesis of a mere solution of such a gas in such a liquid. It seemed conceivable that there might be formed an oxide of silver which was stable at high temperatures, but decomposed on allowing the temperature to fall; a case analogous to the well-known behaviour of silicon trichloride. An attempt has been made to apply a test for the presence in the molten metal of an oxide of silver. It is found that if silver oxide is dropped into melted boron trioxide silver borate is formed, although the temperature is much above the decomposition point of the silver oxide. Accordingly, some highly purified silver was melted in a stream of oxygen, a part only of the surface of the metal being covered with boron trioxide. This procedure was rendered easy by the convexity of the surface of the liquid metal, a ring of the trioxide surrounding the exposed surface. In these circumstances silver borate is formed in large quantity. If, however, the metal is covered entirely, even by a thin film of the trioxide, no silver borate is produced. It cannot be claimed that an absolute proof of the existence of an oxide of silver has been obtained, because there is the possibility of the reaction of three substances together, no two of which will otherwise unite. It seemed worth while, however, to put the experiments on record.

*51. "*The Rate of Transformation of Ammonium Cyanate in Absolute Alcohol.*" By JOHN DAVID MCBEATH ROSS.

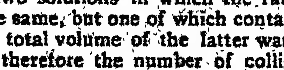
The experiments of Walker and Kay (*Trans.*, 1897, lxxi., 489) on the velocity of the transformation of ammonium cyanate into carbamide in aqueous alcohol have been extended to solutions containing more than 90 per cent of alcohol. On the assumption that the action primarily takes place between the ammonium ions and the cyanate ions, it is found that the acceleration previously observed continues up to alcohol of 99·94 per cent by volume, the increase in the speed of the transformation being most noticeable in solutions containing a large percentage of alcohol. The same conclusions hold good when the action is considered to be primarily due to the non-ionised ammonium cyanate, although in this case the change in the velocity-coefficient is smaller than on the other assumption.

DISCUSSION.

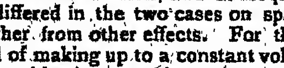
Dr. SENTER referred to the contention of E. E. Walker (*Proc. Roy. Soc.*, 1912, A, lxxxvii., 539) that in determining the influence of alcohol on the rate of decomposition of carbamide in aqueous solution, the solutions should not be made up to a definite volume, but the ratio of carbamide to water should be kept constant and varying proportions of alcohol added. Apart from the objections urged by the author of the present paper, the latter method of making up solutions was open to criticism on kinetic grounds. Comparing two solutions in which the ratio carbamide: water was the same, but one of which contained alcohol in addition, the total volume of the latter was considerably greater, and therefore the number of collisions between the reacting molecules or ions, and consequently the rate of reaction differed in the two cases on spacial grounds, apart altogether from other effects. For this reason the usual method of making up to a constant volume, although not free from objection, would appear to afford a much truer representation of the effect of alcohol on the reaction than the method advocated by E. E. Walker.

*52. "*Condensations of Cyanohydrins.* Part II. *The Condensation of Chloralcyanohydrin with Chloral Hydrate and with Bromal Hydrate.*" By HORACE LESLIE CROWTHER, HAMILTON MCCOMBIE, and THOMAS HAROLD READE.

The compound described by Wallach (*Annalen*, 1874, clxxiii., 297) and Cech (*Ber.*, 1876, ix., 1020) as being formed by the action of potassium cyanide on excess of chloral hydrate has been shown by the authors to have the constitution (I.). In this reaction it is produced by the condensation of normal chloralcyanohydrin (which is first formed) with 2 molecules of chloral hydrate. This condensation has been shown to take place in the presence of potassium hydroxide. Further, using the same condensing medium, the authors have been able to condense chloralcyanohydrin with bromal hydrate with the production of compound II.:—



I.

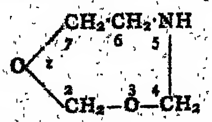


II.

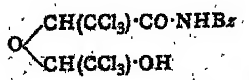
It has been decided to call the parent seven-membered ring (III.) 1:3:5-*dioxazseptan*, so that (I.) is called 6-*keto*-2:4:6-*tri*(*trichloromethyl*)-1:3:5-*dioxazseptan*.

The dioxazseptan derivatives give rise to monoacyl derivatives, in which the acyl group is attached to the nitrogen atom. The benzoyl derivatives when treated

with hydrochloric acid, in glacial acetic acid, are decomposed, one chloral (or bromal) residue is eliminated from the molecule, and there results, in the case of the benzoyl derivative of (I.), *β-trichloro-α(3′-trichloro-α′-hydroxy-ethoxy)-propionobenzamide* (IV.):—



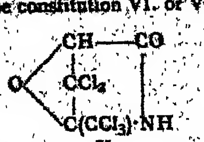
III.



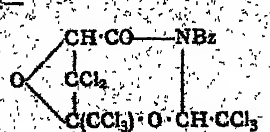
IV.

This compound, on treatment with sodium carbonate, or hydroxide, yields 4:4-*dichloro-3:5-oxido-5-trichloromethyl-2-pyrrolidone* (V.), a compound which is readily soluble in alkalis, but is precipitated unchanged on the addition of acids. An analogous compound can be prepared from the benzoyl derivative of II.

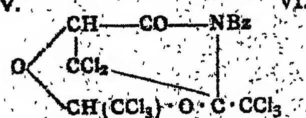
Another interesting change which is undergone by the benzoyl derivatives is brought about by the action of dilute potassium hydroxide. In this case 1 molecule of hydrogen chloride is eliminated, and the resulting compound has the constitution VI. or VII.:—



V.



VI.



VII.

53. "*The System: Ethyl Ether—Water—Potassium Iodide—Mercuric Iodide.* Part II. *Solutions Saturated with Respect to Solid Phases in the Four-component System.*" By ALFRED CHARLES DUNNINGHAM.

The equilibria are represented by means of a tetrahedron, of which a diagrammatic projection was shown. Saturation surfaces exist for the solid phases: potassium iodide, potassium mercuri-iodide, potassium mercuri-iodide hydrate ($KHgI_3,H_2O$), and mercuric iodide. The surfaces are divided by binodal curves into homogeneous and heterogeneous areas, on which liquid mixtures, in equilibrium with the solid phase, exist as one or two layers respectively.

In the case of potassium iodide and potassium mercuri-iodide, the homogeneous portions of the saturation surfaces are entirely separated by a heterogeneous area. This corresponds with the fact that in contact with either of these phases, water and ether are only miscible to a very limited extent.

In the case of potassium mercuri-iodide hydrate and mercuric iodide, the saturation surfaces are divided into homogeneous and heterogeneous portions by critical curves. The homogeneous portions thus formed extend almost across the tetrahedron, corresponding with the fact that in contact with these phases water and ether can become miscible in almost all proportions.

54. "*The Connection between the Dielectric Constant and the Solvent Power of a Liquid.*" By WILLIAM ERNEST STEPHEN TURNER and CRELLYN COLGRAVE BISSETT.

In a series of investigations on the factors affecting the solubility of electrolytes, Walden (*Zeit. Phys. Chem.*, 1906, lv., 683) drew the conclusion that a parallelism exists between dielectric constant and solvent power, and later (*Zeit. Phys. Chem.*, 1908, lxi., 633) formulated an expression, $\epsilon/\sqrt[3]{\mu}$ = constant, applicable to tetraethylammonium and tetrapropylammonium iodides dissolved in a number of solvents, ϵ representing the dielectric constant of the solvent, and μ the molecular percentage solubility of the solute.

It was now shown that this expression is not generally valid, and does not apply to the solubility data of Peddle and Turner (*Trans.*, 1913, ciii., 1202) or of Turner and Bissett (*Trans.*, 1913, ciii., 1904), and on investigation with additional solvents it does not apply, as Walden considered it did, to tetrapropylammonium iodide. An attempt to find another equation was unsuccessful, and it was pointed out that the order of solvent action is in many cases not the order in which the dielectric constants run. Solvent action depends both on the nature of the solute and on that of the solvent.

It was further shown that the solvent action of a number of liquids on *p*-nitrobenzyl chloride and trimethylamine, as measured by Halban (*Zeit. Phys. Chem.*, 1913, lxxxiv., 129), and on carbon dioxide and nitrogen (Just, *Zeit. Phys. Chem.*, 1901, xxxvii., 342), is not connected with their dielectric constants.

55. "*The Viscosities of some Binary Liquid Mixtures Containing Formamide.*" By ERNEST WYNDHAM MERRY and WILLIAM ERNEST STEPHEN TURNER.

The viscosities of mixtures of formamide with water, methyl and ethyl alcohols, formic, acetic, propionic, and *n*-butyric acids have been determined at temperatures of 25° and 40°. From the results of the investigation it was concluded that:—(1) Formamide and the lower alcohols give viscosity curves differing little from the straight line, but as the series is ascended, the calculated and observed viscosities differ by a value which is at first negative and later becomes positive, until, with *iso*amyl alcohol, a curve is obtained which contains a maximum point. The experimental values in the last case were drawn from those of Drucker and Kassell (*Zeit. Phys. Chem.*, 1911, lxxvi., 367).

2. Formamide and the aliphatic acids give viscosity curves resembling in general character those obtained with aqueous solutions of these acids, there being no maximum point with formic acid, although the calculated values are less than the observed. In the other cases, maximum points were obtained on the curve.

3. Maximum points on viscosity curves are not always due to the formation of compounds, and that, in consequence, viscosity measurements do not form a trustworthy method of testing for the formation of compounds in solution.

4. With a series of associated similarly constituted liquids, each mixed with a common associated liquid, the observed viscosity departs more and more from the calculated value as the molecular weight increases in the series.

56. "*The Conversion of* d-*Glucosamine into* d-*Mannose.*" By JAMES COLQUHOUN IRVINE and ALEXANDER HYND.

A detailed account of an investigation, the results of which have already been communicated in the form of a preliminary note (*Proc.*, 1913, xxix., 306).

57. "*The Catalytic Activity of Acids in Ethyl-alcoholic Solutions.*" By HARRY MEDFORTH DAWSON and FRANK POWIS.

Measurements of the rate of isomeric change of acetone under the catalytic influence of acids have been made in ethyl-alcoholic solution. From similar experiments in aqueous solution (*Trans.*, 1913, ciii., 2135) it was previously found that the catalytic effect of the acid can be represented as the sum of effects produced by the ionised and non-ionised acids. The data for alcoholic solutions also indicate that the "hydrogen ion" is not the only active component, but that the non-ionised acid is also possessed of considerable catalytic power.

It was shown that the observations in aqueous solution afford no information as to the real nature of the ionic catalyst, but that some light is thrown on this question by a comparison of the phenomena of catalysis in water and alcohol. If a comparison is made between aqueous and alcoholic solutions of acids according to their electrical conductivity, in which the acids are ionised to about the same extent, it is found that the speed of the catalysed reaction in alcohol is many hundred times greater than in

water. This is explained by the assumption that the active ionic catalyst is the free hydrogen ion which is present in very small concentration in aqueous solutions of acids, but in relatively much greater concentration in alcoholic solution. The retarding influence of small quantities of water on the velocity of this and other reactions in alcoholic solution is in agreement with this hypothesis.

58. "*Heats of Evaporation; Association in Liquids and Mixtures of Liquids.*" By JAMES RIDDICK PARTINGTON.

The equation of Bakker for the latent heat of evaporation of a liquid, which is deduced from the characteristic equation of van der Waals, gives results in poor agreement with experiment. It was shown that the characteristic equation of D. Berthelot leads to an equation giving results in much closer agreement with the experimental numbers. The equation is:—

$$\lambda = \frac{27}{64} R^2 \frac{T_k^2}{p_k v_1 T_1} + RT_1,$$

where λ is the molecular heat of evaporation at the tem- T_1; v_1 is the molecular volume of the liquid; p_k, T_k are the critical pressure and temperature, and R is the gas-constant.

Some thermal properties of liquid mixtures were considered from the point of view of thermodynamics.

PHYSICAL SOCIETY.

Ordinary Meeting, February 27, 1914.

Prof. Sir J. J. THOMSON, O.M., F.R.S., President, in the Chair.

THE PRESIDENT opened the meeting by calling upon Prof. G. CAREY FOSTER, who gave a short biography of Prof. Frederick Guthrie, to whom the Physical Society of London owed its initiation. Guthrie was born in 1833 and died in 1886. Like many others who had attained to distinction in Physics, he began as a chemist. He was practically the sole founder of the Society, which held its first meeting in the spring of 1874 in his own lecture theatre in the Royal School of Mines in Exhibition Road. He usually wore a grave and solemn appearance, which made him look much older than he really was, but those who knew him were aware of the warm kindliness and the fund of twinkling humour which lay beneath.

Sir OLIVER LODGE said that his only claim to address them on this occasion was that he had been a student of Prof. Guthrie and also of Prof. Carey Foster. To the students Guthrie appeared a portentous senior, and he (the speaker) used to regard him as nearer eighty-five years of age than fifty. He thought it most appropriate that the Society should have inaugurated this series of lectures to commemorate its connection with Prof. Guthrie.

The PRESIDENT, in introducing Prof. R. W. WOOD, of Johns Hopkins University, Baltimore, as the first Guthrie Lecturer, referred to his unrivalled skill as an experimenter, and congratulated the Society on having obtained his services on this occasion.

Prof. R. W. WOOD then delivered the first Guthrie Lecture on "*Radiation of Gas Molecules Excited by Light.*"

The emission and absorption of light by molecules and the allied phenomenon of dispersion have led us to the conception of something within the atom which is capable of responding to light waves in much the same way as a tuning-fork responds to sound waves of the same frequency as its own, and many mathematical treatments have been built up which explain more or less perfectly many of the phenomena in question. These still leave us very much in the dark as to what is going on. Helmholtz explained absorption by introducing a frictional term into his equations of motion for the atom, and though this led at once to an expression which represented anomalous dispersion, it left us ignorant of how the energy absorbed by the molecules was transformed to heat, or how the mean velocity of the molecules was increased by the excitation of vibrations within them. Planck avoided this difficulty by considering that the energy abstracted from the beam of light is re-emitted, though at the time the only experimental evidence was to be found in selective reflection, which occurs only in liquids and solids.

What becomes of the absorbed energy in the case of a gas? This was what he had been asking himself for many years. While he did not require a working model of the atom, he could not, however, be satisfied by an equation in which absorption was represented by a frictional term or selective reflection predicted by the ocurrence of an imaginary quantity.

The problem of the constitution of the atom is one which must be approached from many sides, as it is improbable that any single mode of attack will reveal the secret. The spectroscope alone has proved itself powerless, one great difficulty being that in all known methods of exciting spectra one got "the whole or nothing."

Flames, arcs, sparks, and vacuum-tube discharges set a host of vibrations simultaneously in operation within the atom, and resulted in a complex of lines which were difficult to interpret.

His line of attack had been to maintain the molecules in as calm and tranquil a state as possible, by keeping them cool, and then to excite them to radiation by the application of an alternating electromagnetic field of a definite frequency—usually called monochromatic light. That this method has in some degree simplified matters was proved by the fact that sodium vapour could be made to emit only one of the D lines instead of the usual two.

The conditions necessary to stimulate radiation in this way varied considerably with the nature of the element studied. He would begin, however, with the simplest case, that of a vapour which exhibits a single absorption line and emits radiations similar in every respect to the exciting radiations when stimulated by light of frequency equal to that of the absorption line. This condition was perfectly fulfilled by the vapour of mercury, which has an absorptine line at $\lambda = 2536$ in the ultra-violet.

If a beam of monochromatic light of this wave-length was focussed at the centre of an exhausted quartz bulb containing a drop of mercury at atmospheric temperature, it was found that the light was powerfully scattered by the vapour, photographs of the bulb made with a quartz lens showing the cone of rays much as if the bulb were filled with smoke. The scattered light is invariably much more homogeneous than the incident beam, in which the "line" has a finite width, whereas the scattered light corresponds only with the centre of this line. The rest gets through the vapour unaffected. With the light thus scattered—the *Resonance Radiation*—a photograph was made of a quartz bulb containing a minute drop of mercury at room temperature. The bulb appeared as if filled with ink owing to the opacity of the vapour for the rays.

These phenomena, visible only to the camera, can be visually reproduced in the case of sodium vapour excited by the light from a sodium flame. If the density of the vapour is increased by warming it, the distance which the light can penetrate into the bulb is diminished and eventually the resonance radiation is all emitted from a region so close to the surface that it appears as a bright yellow patch on the inner surface of the glass.

If this patch is now used as a lamp, and focussed by a concave mirror on the surface of the same globe (or another in which the vapour is of sufficient density to give the patch effect) so as to fall partly on a surface whitened by deposited magnesia and partly on the enclosed vapour, the brightness of the two contiguous patches thus formed is practically equal.

This proves that, under those conditions, at comparatively low densities, *true absorption does not exist*, the light abstracted from the incident beam being re-emitted as light of the same wave-length but in all directions.

The factor of true absorption makes itself manifest as soon as we admit air or some other foreign gas. Even if

the pressure is only a millimetre or two the effect is very marked.

Another point which can be brought out by this method of attack is whether or not the mechanisms whose vibration frequencies correspond to the various lines in a spectrum are independent of each other or are interconnected.

An ingenious method was described whereby a beam of considerable intensity, consisting however of only D_1 *or* D_2 light, could be obtained, and if the sodium vapour excited by either of these was examined spectroscopically the emitted light contained only that one of the lines which was used to excite it. This shows that the D_1 and D_2 mechanisms are quite independent. In other cases, however, vapours excited by light of any one line of their spectrum gave out a resonance spectrum of that line and one or more others showing that some groups of mechanisms were inter-dependent and could not be excited separately.

Stimulation by Waves of very Short Wave-length.—Experiments were then described in which air, nitrogen, &c., had been caused to emit ultra-violet light when exposed to the action of radiation of wave-length less than the Schumann rays, the smallest waves hitherto known. Schumann rays were completely absorbed by quartz, but would pass through a considerable thickness of fluorite, but the rays to which he referred could be reduced in intensity by 98 per cent by a plate of fluorite 1 mm. thick. Nitrogen was more actively stimulated than air by these rays, as oxygen seemed to have a destructive effect on the phenomena. Thus iodine vapour, if mixed with nitrogen, emitted a green light under the action of the rays, while remaining dark if mixed with oxygen.

He urged the necessity of an exact mathematical treatment of the phenomenon of a molecule of vapour re-emitting radiation which it has abstracted from an incident beam, true absorption being absent.

At the conclusion of the lecture a number of interesting experiments illustrative of the subject of the lecture were shown. These included the resonance radiation of sodium stimulated by D light, of iodine vapour stimulated by the light from a quartz mercury lamp, and of the author's method of extinguishing one of the D lines from the light from a sodium flame.

SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

Ordinary Meeting, March 4, 1914.

Mr. A. Chaston Chapman, President, in the Chair.

Messrs. Rowland Holliday Ellis and Armand de Waels were elected Members of the Society.

Certificates were read for the first time in favour of Messrs. Lauchlan Henry Dyke Acland, 55, Comeragh Road, West Kensington, W.; Frederic Herbert Lees, 31, Summerhill Road, Dartford, Kent; William Henry Woodcock, 132, Felbrigg Road, Goodmayes, Essex; Walter Alan Gibbings, P.O. Box Sannomiya 174, Kobe, Japan.

Certificates were read for the second time in favour of Messrs. Robert Bickerstaffe, Thomas Henry Byrom, Sydney George Clifford, Donald Richard Frazer, and John McLaren.

The following papers were read:—

"*Composition and Analysis of Compound Liquorice Powder.*" By Albert E. Parkes and Frederick Major.

The authors suggest a method of chemical examination of compound liquorice powder whereby an idea may be obtained of the quality of each ingredient. Results obtained by this method from a number of commercial samples and standard samples made up from ingredients of known purity are given.

"*Composition of the Saline Matter Adhering to certain Wet Salted Skins.*" By M. C. Lamb.

Large numbers of goat skins, primarily intended for the manufacture of glacé kid, are exported from India, which are "cured" with a natural salt earth applied to the flesh side. An analysis of the adhering saline matter shows that this consists primarily of sodium sulphate, and contains only comparatively small traces of common salt.

"*Determination of Carbon Monoxide in Air.*" By F. S. Sinnatt and B. J. Cramer.

A method for the determination of carbon monoxide in air is described which depends upon the oxidation of the gas by means of iodine pentoxide; the carbon dioxide produced is collected in an evacuated vessel, the flow of the gas being controlled by an apparatus described by Sinnatt (*Analyst*, 1912, xxxvii., 12). The carbon dioxide present in the resulting gas is estimated by Pettenkofer's process in a similar manner to that used in air analysis.

"*Standardisation of Dried Carica Papaya Juice, the Active Principal of Papain.*" By F. T. Shelley.

The method of standardisation is a slight modification of Sörensen's method of measuring the amino acids formed in an alkaline solution of pure casein. After a digestion of four hours in an incubator at 37° C., using phenolphthalein as an indicator, 0·04 grm. should produce amino-acids equivalent to at least 1 cc. of N/5 alkali.

INSTITUTE OF CHEMISTRY.

At a meeting of the Institute of Chemistry held at King's College, London, on Thursday, February 26, 1914, Prof. R. Meldola, President, in the Chair, Mr. William Macnab delivered the first of two lectures on "*Explosives.*"

He said that since the discovery of gunpowder, in the thirteenth century, man had always been trying to make explosives do work for him either for military or engineering purposes.

Whatever opinions might be held as to the use of explosives in war, there could be no difference of opinion as to the benefits reaped from the use of industrial explosives, which had lightened and expedited the work of the engineer and miner to an enormous extent.

Remarkably little alteration had been made in the composition of gunpowder, which was the explosive in practical use until about forty years ago, when cocoa or brown prismatic powder was produced to meet the requirements of the larger guns which were being made.

The discovery of guncotton had led to great hopes of more efficient explosives for guns and blasting being available, but there were so many serious accidents and it was so unreliable in its behaviour that for a number of years little progress was made. Abel first made guncotton, a really serviceable explosive, by devising the process for treating it in a paper pulping machine, which reduced the fibres of the guncotton to a very fine state of division, which enabled the acid to be thoroughly washed out and a sufficiently stable material produced.

When Nobel began to make nitro-glycerin as a blasting explosive, a new era commenced; his skill and inventiveness rapidly overcame the dangers and drawbacks which first surrounded its manufacture and use, and it had now become the main constituent of the blasting explosives most widely used.

To Vieille belonged the credit of making the first reliable smokeless powder for guns, by thoroughly gelatining nitro-cellulose, and Nobel succeeded in taming the two violent explosives, nitro-glycerin and nitro-cellulose, by gelatining them together, and producing a safe and powerful propellant. These two powders were the starting-point for all the smokeless powders subsequently produced.

The various types of other explosives were described, including the combinations of ammonium nitrate with aromatic nitro-compounds, &c., and those containing chlorates and perchlorates.

The two modes of explosion—combustion and detonation—were discussed. Gunpowder was mentioned as an instance of the first class, called a "low" explosive; in contradistinction to dynamite, which was a detonating and "high" explosive. The velocity of the explosion wave in dynamite was 6000 metres per second.

After explaining the chief principles underlying explosive reactions, the lecturer described the various methods and apparatus used in the examination and study of explosives, as well as the difficulties in controlling and retaining in vessels the products of explosion where very high temperatures and pressures of many tons to the square inch were developed.

The detonator was an important item in connection with blasting explosives, for it served to fire and develop the full force of the "high" explosive class. For many years fulminate was the chief ingredient of the detonator charge, but now trinitrotoluol, or picric acid, or tetranitromethylaniline was used as the chief ingredient, with a small priming charge of fulminate, and more recently lead azide and also tetranitroaniline had been tried.

Increased power could be obtained by the use of a detonating fuse of trinitrotoluol inserted alongside of the charge of explosive, especially in deep holes, as the trinitrotoluol detonated with greater velocity than the blasting charge, and caused it to explode more simultaneously than when ordinarily fired by a detonator placed in the top cartridge.

In the next lecture it is proposed to deal more especially with the manufacturing side of the subject, and the restrictions under which the works must be constructed and the operations carried on.

NOTICES OF BOOKS.

Allen's Commercial Organic Analysis. Volume VIII. Fourth Edition. Entirely Re-written by W. A. Davis, B.Sc., A.C.G.I., and Samuel S. Sadtler, S.B. London: J. and A. Churchill. 1914.

This volume completes the fourth edition of Allen's invaluable work, but a supplementary volume is to be issued shortly containing the latest results which have been published since the revision was first taken in hand. The eighth volume deals with the analysis of meat and milk products, proteins, and albuminoid substances, hæmoglobin and blood, proteoids and fibroids, and an introductory article by Prof. E. Frankland Armstrong on enzymes has been added. A great deal of fresh material has been incorporated in the new edition, which has undergone such extensive revision that it is practically a new work. For the sake of completeness a certain amount of matter dealing with the separation of amino acids is included, which duplicates some parts of the text of volume vii., but the editors considered it advisable to retain it in both volumes, for the information is presented to the reader from two quite different points of view.

The Art of Dying. Published by the Tapestry Studio, Shottery, Stratford-upon-Avon.

This is a reprint of an old book upon the art of dyeing and contains a number of recipes and directions for producing different shades upon various materials. It consists of two parts, the first of which was translated from the German, and gives "an experimental discovery of all the most useful secrets in dying silk, wool, linnen," while Part II., translated from the French, contains general instructions for the dyeing of wools and woollen manufactures. The original spelling of the first edition, published in 1705, has been preserved, and all who are interested in the history of dyeing, and the development of the art, will find the study of the book both profitable and entertaining.

A Text book of Chemistry. By William A. Noyes. New York: Henry Holt and Co. 1913.

The author of this book has had the requirements of two classes of college students in view, namely, those who have been through an elementary course of chemistry at school and are continuing the subject at college, and, secondly, those who are beginning the study of chemistry after having done only a little work in physics at school. The book will probably be found more useful by the former class than the latter, the order in which the subject is presented being distinctly more suitable for those to whom it is not entirely new. Thus a good deal of rather difficult theoretical work is introduced early in the text, the atomic theory being discussed at the very beginning, and catalysis, electrolysis, and the kinetic theory when only hydrogen and oxygen have been studied. Throughout the book Prof. Ostwald's device is adopted, and paragraphs dealing with more advanced subjects are marked with an asterisk. The usual ground in inorganic chemistry is, on the whole, quite adequately covered, and many examples which will give plenty of practice in calculation are included.

Radioattività ed Atomi. ("Radio-activity and Atoms"). By Prof. Giuseppe Oddo. Pavia: Prem. Stab. Tip. Successori Bizzoni. 1914.

This pamphlet contains the inaugural lecture delivered by Prof. G. Oddo before the University of Pavia at the beginning of the Academical year 1913-1914. The lecturer gave a particularly interesting account in language which was as far as possible non-technical of the history of the discovery of radio-activity and of the subsequent development of the subject. The account was thoroughly up-to-date, most recent work being noticed in it, and modern theories of the structure of the atom were tersely described. The bibliography given in the pamphlet contains the titles of all works of importance dealing with radio-activity published in English, French, German, or Italian.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clviii., No. 3, January 19, 1914.

Application of Spectroscopy to the Study of Chemical Equilibria. Systems formed by Oxalic Acid and Salts of Uranyl.—Victor Henri and Marc Landau.—A mixture of oxalic acid and salts of uranyl absorbs the ultra-violet rays much more than the sum of its constituents. The increase of absorption produced by oxalic acid is greater for the sulphates and nitrates of uranyl, less for the chloride, and still less for the acetate. The acetate and oxalate of uranyl absorb the ultra-violet rays more than the chloride, nitrate, and sulphate. This result confirms the general rule that the presence of two chromophore groups in a molecule produces an increase of absorption which is greater than the sum of the absorptions of each chromophore. In the present case the chromophore groups are UO_2· and COOH. There is a direct relation between the photocatalytic power of salts of uranyl and the exaltation of the absorption produced by the salts on oxalic acid.

Berichte der Deutschen Chemischen Gesellschaft. Vol. xlvii., No. 1, 1914.

Tellurium-carbon Sulphide, CSTe.—Alfred Stock and Paul Praetorius.—By the pulverisation of electrodes of mixtures of tellurium and graphite under carbon disulphide, tellurium-carbon sulphide, CSTe, and non-volatile

decomposition products of CS_2 and also C_3S_2, carbon subsulphide, are formed. The decomposition products are readily separated by distillation, while to free the CSTe in solution from the C_3S_2, two methods are available:—(i.) Repeated fractional extraction of the solutions with currents of CS_2 vapours; (ii.) conversion of the C_3S_2 into a non-volatile substance and subsequent distillation. It is best to employ both methods, using β-naphthylamine as reagent in the second case. All experiments with CSTe solutions must be performed in absence of daylight or bright artificial light, as the compound and its solutions are extraordinarily sensitive to light. The melting-point of the pure substance is $-54°$. Its solutions are reddish brown, red, or yellow, according to their concentration. It has a characteristic smell like garlic. It is very unstable, readily giving black condensation products.

Selenium-carbon Sulphide, CSSe.—Alfred Stock and Ernst Willfroth.—Selenium-carbon sulphide, CSSe, like tellurium-carbon sulphide, can be prepared in the form of a carbon disulphide solution by the electrical pulverisation of selenium graphite electrodes under CS_2. The C_3S_2 formed can be removed by fractional distillation in a current of CS_2 and subsequent treatment with β-naphthylamine. CSSe decomposes when exposed to light, heated, or kept for some time at room temperature. It is readily decomposed at higher temperatures, carbon diselenide not not being formed.

Magnesium Chloride as Mineralising Agent, with a Contribution to the Spectro-chemistry of the Rare Earths.—K. A. Hofmann and Kurt Höschele.—Fused anhydrous magnesium chloride is an excellent solvent and crystallising agent for many inorganic oxides. Thus of the spinels magnesio-ferrite, $(FeO_2)_2Mg$, is readily obtained in the crystalline form. Magnesium chloride when fused acts upon the oxides and sulphates of the coloured rare earth metals to give the crystallised oxychlorides. When the absorption spectrum of erbium oxychloride is examined it is found that it does not differ from those of the amorphous chloride and oxide. Thus the light-absorbing electrons of the erbium atom are not affected when the principal valencies are called into play by chlorine or oxygen. The same result is obtained with neodymium and praseodymium oxychlorides.

Electrolytic Reduction of Carbon Monoxide and Carbon Dioxide Dissolved under Pressure.—Franz Fischer and Oskar Prziza.—When carbon dioxide is dissolved under pressure it can be reduced quantitatively to salts of formic acid with currents of high density (10—15 amp. per sq. dm.). But high concentrations cannot be obtained because the anion of the formic acid soon begins to migrate towards the anion. With currents of low density carbon monoxide dissolved under pressure can be reduced to methyl alcohol, but the yields are poor. Methane is apparently not formed.

MEETINGS FOR THE WEEK.

Monday, 16th.—Royal Society of Arts, 8. (Howard Lecture). "Surface Combustion," by Prof. W. A. Bone, F.R.S.

Tuesday, 17th.—Royal Institution, 3. "Modern Ships," by Prof. Sir John H. Biles, D.Sc., &c.

Wednesday, 18th.—Royal Society of Arts, 8. "House Flies and Disease," by Dr. E. H. Ross.

Thursday, 19th.—Royal Institution, 3. "Heat and Cold," by Prof. C. F. Jenkin, M.A.

—— Royal Society of Arts, 4.30. "Indian Water Gardens," by Mrs. Patrick Villiers-Stuart.

—— Royal Society. A Discussion on "The Constitution of the Atom" will be opened by Sir Ernest Rutherford, F.R.S.

—— Chemical, 8.30. "Ignition of some Gaseous Mixtures by the Electric Discharge," by H. F. Coward, C. Cooper, and J. Jacobs. "Deliquescence—Part I., The Deliquescence of Salts of Ammonium Bases," by C. J. Peddle. "Hydrazoximes of Methyl- and Phenyl-glyoxals," by B. B. Dey.

Friday, 20th.—Royal Institution, 9. "Fluid Motions," by The Rt. Hon. Lord Rayleigh, O.M., F.R.S.

Saturday, 21st.—Royal Institution, 3. "Recent Discoveries in Physical Science," by Prof. Sir J. J. Thomson, O.M., F.R.S.

THE CHEMICAL NEWS.

VOL. CIX., No. 2834.

MAGNETIC SUSCEPTIBILITIES OF THE ELEMENTS.

By F. H. LORING.

(Concluded from p. 123).

PROF. EWING gives some interesting examples. Soft annealed wrought-iron, before hardening by stretching, has a maximum susceptibility $k = 245$; after stretching, the maximum value falls to 55, the intensity of magnetisation (I) being in each case about 650. Nickel-rod annealed has a maximum permeability of about 350, B being about 2300, but in this case the specimen was under compression stress. In its normal state $\mu = 225$, B being about 1500. Similarly, *cast* cobalt under a certain compression stress has a permeability of 260, B being about 3750; without compression stress $\mu = 200$, the induction (B) being about the same.

From my own studies in atomic weight relations it seems probable that the magnetic properties of the elements can be brought into systematic relationship, and to this end I shall have to refer to some of my early papers describing an elliptical method or system of treatment published in the CHEMICAL NEWS (1909, xcix, 148 and 241).

The table shown on p. 241 may, in some respects, be improved by introducing a fresh curve, and making a slight re-arrangement as here shown by Table IV.

To keep such an arrangement of values (elements) in harmony with another method, that of the quaternian series which I have developed, or with the values of these series (see CHEMICAL NEWS, 1913, cviii., pp. 95, 188, 247, and 305), some slight transpositions of a few of the elements (atomic weights) were rendered necessary. There is much uncertainty in these relations, however.

Nevertheless, Table IV. may be utilised to bring out the magnetic relations here considered, but, before submitting these for study, an explanation of the table will be given. The rows of numbers, A and B, represent the successive ellipses which carry or intersect the elements (atomic weights) as shown, the elements occurring in more or less regular groups. The acid-forming elements are arranged uppermost, and those belonging particularly to rows *a*, *b*, *c*, and *g*, *h*, *i*, *j*. The base-forming and peroxide-forming (non acid-forming) elements are, for the most part, arranged undermost, being represented in rows *d*, *e*, and *k*, *l*. Manganese having marked extreme properties is dually placed as shown, a gap being available.

There appears to be no peroxide of gold, but the position of this element is justified by that given to silver, inasmuch as there is some tendency for the elements occupying similar but uniformly displaced places to have some common or allied characteristics, as instanced by bromine and iodine. A few connecting lines are inserted to characterise this relationship. More might be added, but it will be seen that this method of association leaves much to be desired.

The inactive gases are placed outside the system proper, but they may be regarded as belonging to, or stepping down from, the places indicated by the letter X, without, of course, a change in atomic weight. Beryllium and nitrogen are irregular in the system. The relative positions of a few elements like those of carbon and oxygen may be reversed.

In the disposition of the elements in Table IV. it will be seen that there is a pronounced tendency of the hard or high melting-point elements to alternate with those having a low melting-point and of a soft character. For example:—

P = soft, V = hard, Br = soft (liquid), Mn = hard, &c.; or C = soft (graphite), Sn = hard, I = soft, Mo = hard, &c.

or, again, P = soft, Li = hard (relatively), Zn = soft, V = hard, &c.

TABLE IV.

a.	F										
b.	Cl−									Si ± ?	
Be +											
c.	B−		P−	V+	Br−	Mn+	Se−	Nb+	As−	Mg+	
d.	Al+	X	Fe+	Cu−	Ga	Co+	Ge	Yt−	X	Ni+	
e.	H−	Na+	Li+	Zn−	K+	[Mn+]	Sr	Rb+	Ru+	Ag−	
f.	Ar−									Kr	
	1	2	3	4	5	6	7	8	9	10	A
g.	S−										
h.	Te−								Eu+		
i.	Ti+	C−	Sn+	I−	Mo+	Sb−	Ta+	? Ct	? Lu+		
j.	Rh+	O+	Cr+	In	Gd	Er+	? Ny+	Tm+	Dy+		
k.	Sc−	X	Pd+	Cd−	Pr+	Ho+	Nd+	X	Ir+		
l.	Zr−	Ca	Ba	Cs	La−	Tb+	Ce+	Sa+	Au−		
		Ne			Xe			"Y"?			
	1	2	3	4	5	6	7	8	9	B	

Notes.

Indium in a field below about 7 kilogauss (7000 lines per square centimetre) was found to have a *positive* susceptibility, whilst above 7 kilogauss the susceptibility became *negative*. The maximum susceptibility given on either side of the zero was of the order of 0.10×10^{-6}. Iron may have been present as an impurity, however.

The susceptibility of tin at temperatures throughout a considerable range below 233° C. is *positive*, whilst at higher temperatures, from 250° upwards, the susceptibility is *negative*, being about -0.04×10^{-6}. The positive susceptibility is of the same order, and both are *constant* for a range of varying temperatures on each side of the sharp descent through zero, *i.e.*, from these temperatures given, in either direction. The field strength = 10.5 kilogauss, a strength employed by Honda for many measurements under conditions of varying temperature.

Fluorine, gallium, and strontium are possibly diamagnetic. Cæsium and barium probably are close to zero.

Or, regarding the elements as metallic and non-metallic in character, these properties are seen to alternate in rows c and i; compare the magnetic properties.

Mention should be made of the elements of the rare earth group, as it has been supposed that some of these in a pure state will be appreciably or even very strongly magnetic, judging from the relatively high susceptibilities of some of their oxides of the type R_2O_3. The work of B. Urbain and G. Jantsch (*Comptes Rendus*, 1908, cxlvii., 1286) on these oxides indicates positive values for $k \times 10^6$ as follows:—Nd = 35·5, Sa = 6·5, Eu = 33·5, Gd = 161, Tb = 237, Dy = 290. La is diamagnetic and Pr is paramagnetic, whilst Ho has a very high susceptibility, and Er, Tu (or Tm), Ny (or Yb = Ad) and Lu (= Cp) are successively lower, the values and comparisons given being for the oxides. The two last-named elements have the values respectively, 18·3 and 3·78 for their oxides, according to S. Meyer (*Akad. Wiss. Wien. Sitz. Ber.*, 1908, cxvii., 2a, pp. 995—1000). This experimenter states that the metallic powders of Yt, Er, and Ho (mixtures) were not much more magnetic than their corresponding oxides, but they showed distinct remanence, and highly magnetic alloys may be yet possible with some of the elements of this group.

Honda and Sone (*Imp. Univ. Tôkohu Sci. Reports*, 1913, ii., No. 1, pp. 25—31), in a recent investigation on erbium (powder), find the value to be +22·4, so that this element would come next to manganese in Table II. Their investigations of the following elements will be of interest:—Diamond (dodecahedron) = −0·452; diamond (octahedron) = −0·438; sulphur (rhombic) = −0·476; sulphur (stick) = −0·444; sulphur (powder) = −0·416; manganese = +9·7 to +10·1; rubidium (regulus) = +0·088; selenium (metallic) = −0·304; osmium (powder) = +0·074; graphite (Ceylon No. 1) = −12·2 to +0·28, depending upon its axial positions, &c., in the field. At a temperature of 1200° the susceptibility of the graphite was reduced to one-fifth of its original value; on cooling below 600° it began preceptibly to decrease, and at 390° zero susceptibility was reached, which passing through the zero became $+6·8 \times 10^{-6}$ at laboratory temperature. The change at 600° corresponds roughly with the magnetic transformation temperature of iron, pointing to the presence of iron as a conditioning impurity. For diamond, graphite, sulphur, manganese, and osmium the susceptibility was independent of the field strength.

Some of the rare-earth metals, and one or two others, are arbitrarily inserted in Table IV., as a reminder that they must ultimately be dealt with in any complete scheme. Germanium in particular is arbitrarily placed. All the atomic weights of these elements are not known accurately in the first decimal place; indeed, some are not known to within nearly one whole unit. Those elements which do not appear in the special table are of high atomic weight, and they may be members of another (3rd) grouping.

The magnetic susceptibility of the weakly magnetic elements is, owing to the feebleness of the effect, profoundly influenced by the presence of impurities, such as iron, and no doubt the physical state of the substance (see carbon) is also a factor which sometimes renders the values in question in some degree uncertain, or unsatisfactory for close comparative purposes. In these tables many of the values were obtained by Honda (in co-operation with H. E. J. G. du Bois), and for purposes of comparison such values may be given a preference (see Honda, *Ann. Physik.*, 1910, xxxii., 1027). In the Landolt-Börnstein compilation references are given, and for a detailed study of the subject the original papers should be consulted.

Chemical Society.—The Annual General Meeting of the Chemical Society will be held on Thursday, March 26, 1914, at 4.30 p.m., when the President (Prof. W. H. Perkin, F.R.S.) will deliver his Address, entitled "Recent Researches on Tautomerism."

THE DETECTION OF TRACES OF COPPER.*

By WESLEY B. PRITZ, A. GUILLAUDEU, and JAMES R. WITHROW.

A FREQUENT feeling of uncertainty regarding the significance of qualitative tests for the completeness of the electrolytic precipitation of copper, made it desirable to know the limits of the sensitiveness of the recommended reagents, as commonly employed. It was also desired to modify, if necessary, the sensitiveness of one of the reagents to meet the requirements of the work on electrolytic precipitation of copper in progress in the Chemical Laboratory of the Ohio University. As it is often essential in electro-analysis to remove only such volume of solution for the qualitative test as will contain an insignificant weight of copper, the method selected must be made applicable to samples not greater than about 1 cc. Of the reagents recommended, the ones which in our experience are in most general use are ammonium hydroxide, ammonium sulphide, and potassium ferrocyanide. Since a study of the sensitiveness of these three, under the conditions in the copper work on hand, showed that ferrocyanide could be made to answer our purpose, other methods were not examined.

Heine appears to have utilised colour for the detection of copper as early as 1830 (*Bergwerksfreund*, i. 33; xvii., 405; *Zeit. Anal. Chem.*, xlvi., 644). Müller, in 1855, with his complement colorimeter using 5 cc. of solution was able to detect 50 parts of copper in 1,000,000, using ammonium hydroxide as reagent (*Journ. Prakt. Chem.*, lxvi., 203). Wagner, in 1881, stated that the blue colour given to solutions of copper salts by ammonium hydroxide will detect 1 part in 25,000 (*Zeit. Anal. Chem.*, xx., 351). Milbauer and Stänek, in 1907, thoroughly investigated this colour, and found that free ammonia and ammonium chloride diminished the intensity, but ammonium carbonate intensified it one-third (*Zeit. Anal. Chem.*, xlvi., 644).

Carnelley, in 1875, found that in acid solution, ferrocyanide will detect 1 part of copper in 1,000,000 parts of water, while in neutral solution the colour changes from brown to brown-purple, and 1 part copper can be detected in 1,500,000 parts (CHEMICAL NEWS, xxxii., 308). The addition of ammonium nitrate or any other ammonium salt greatly increases the depth of colour, making possible the detection of 1 part of copper in 2,500,000 parts. Hydrogen sulphide is also said to detect 1 part of copper in 2,500,000 parts of water. Wagner, in 1881, reported that ferrocyanide will detect 1 part of copper in 200,000 parts of solution (*Zeit. Anal. Chem.*, xx., 349). Nessler and Barth, in 1883, used 10 cc. of solution, and could detect 2 parts in 1,000,000 with the use of potassium ferrocyanide (*Zeit. Anal. Chem.*, xxii., 37). Cooper, in 1886, by using varying depths of solution up to 14½ inches in tubes enclosed in opaque cylinders, claims ability to detect 1 part of copper in 1,950,000 parts of water with ammonium hydroxide, and 1 part in 11,750,000 parts with ferrocyanide (*Journ. Soc. Chem. Ind.*, v., 84). H. Thoms, in 1894, placed the limit of this last test at 1 part in 200,000 (*Pharm. Centralhalle*, xxxi., 31; *Zeit. Anal. Chem.*, xxxiii., 464). Bradley, in 1906, found that potassium ferrocyanide could detect copper in a solution containing 1 part in 100,000, but not in a solution of 1 part per 1,000,000 (CHEMICAL NEWS, xciv., 189).

Such variation in values for the sensitiveness of the reagents mentioned should surely meet any requirements which might arise. We made no attempt to reconcile or judge between any of them, except in so far as our own conditions were concerned. Many other tests have been advanced from time to time, and doubtless have much value in their place. The range of recommendation even in this kind of work is quite broad, but from our point of view somewhat lax. Such tests as raising the level to see

* Read before the Indianapolis meeting of the American Chemical Society. From the *Journal of the American Chemical Society*, xxxv., No. 2.

if fresh copper is deposited (Treadwell-Hall, "Analytical Chemistry," 1905, vol. ii., p. 148; Fresenius-Cohn, "Quantitative Chemical Analysis," 1908, p. 621; Low, "Technical Methods of Ore Analysis," 1908, p. 89; Julian, "Quantitative Chemical Analysis," p. 250; Warwick, *Zeit. Anorg. Chem.*, i., 289), and electrolysing until the solution becomes colourless (Rudörff, *Ber.*, xxi., 3050), do very well in many cases, but frequently are inadequate. We have noticed, for instance, in cases where the test used was the raising of the level of the electrolyte toward the end of a precipitation between insoluble electrodes, and no visible copper was deposited, that there was a sensible lowering of the intensity of the ferrocyanide test made before and then after the rise in level.

Experimental.—The stock solutions used contained 1 part of copper as sulphate in 1000, and also in 25,000 parts. The copper sulphate was "Baker's Analysed" in the last case and iron-free crystals re-crystallised after several precipitations as crystal meal in the other case. In the preliminary experiments, when 1 cc. portions of solution were examined in ordinary test-tubes, the conservative statements in the literature regarding sensibility were confirmed, although somewhat greater sensitiveness could be obtained. In the case of ammonium hydroxide 1 part of copper in 40,000 could be detected, but not with as great certainty as 1 in 25,000. With potassium ferrocyanide in presence of acetic acid the sensitiveness varied roughly inversely as the concentration of the ferrocyanide solution used. One drop of 8·5 per cent ferrocyanide added to 5 cc. of solution in an ordinary test-tube could detect 1 part of copper in 200,000 parts of solution, but not in 300,000 parts. A 3 per cent solution of ferrocyanide added in the same way to 1 cc. portions gave a distinct pink, with a dilution of 1 part in 300,000 and not with 1 in 600,000. The same results were obtained using 2 cc. portions. These results were not as delicate as desired. It was found, too, that slight variations in the procedure when making and examining the tests gave pronounced differences in results. This doubtless has a bearing on the widely varying values on record. In fact, a study of the literature seems to indicate that a major factor in the variations in the recorded values is the lack of uniformity in the quantity of sample used. In our work means of regulating other factors causing difficulty were developed.

Apparatus.—The apparatus finally adopted for detecting traces of copper was an adaptation of the ordinary Nessler tube, and was exceedingly simple. A number of tubes were made, 3 to 5 mm. in internal diameter and up to 15 cm. in length, having a capacity of nearly 3 cc. They were made from ordinary thin-walled glass tubing, one end being sealed and preferably slightly ballooned to avoid thickening. The glass used was the lightest obtainable. When viewed on the end it must not be green, or the delicacy of the tests will be affected. The side-walls of the tubes were wrapped with black paper to exclude all light except that entering the bottom of the tube. This wrapping greatly increased the delicacy of the tests on the weaker solutions. The solution to be tested was introduced into the tube by means of a 1 cc. pipette.

Ammonium Hydroxide Reagent.—Three drops of this reagent (sp. gr. 0·904) were added to the 1 cc. of the solution to be tested, contained in a tube. A blank containing 1 cc. of distilled water and three drops of the hydroxide was also prepared in each case. The two tubes were observed in light thrown up through them from a white screen. N/2500 copper sulphate solution gave an easily distinguishable coloration; with N/3000 the colour was faintly distinguishable, while with N/4000 it could scarcely be distinguished at all. N/3000 was therefore taken as the limit of the sensibility of ammonium hydroxide in the detection of copper in sulphate solutions in such tubes as described. This means that in 1 cc. of electrolyte tested copper may still be detected with the ammonium hydroxide reagent when the electrolyte contains 0·00106 grm. of copper per 100 cc. or 10·6 parts per 1,000,000. This too much copper to leave in the electrolyte when a grm. or less of copper is being deposited.

Ammonium Sulphide Reagent.—This reagent was made in the usual manner and used as the ammonium hydroxide just described. Solutions as dilute as N/20,000 gave evidence of the presence of copper. The colour from N/25,000 solutions could scarcely be differentiated from that of the blank comparison tube. N/20,000 was therefore established as the practical limit of sensibility with ammonium sulphide. This means 0·00016 grm. copper per 100 cc. of solution when 1 cc. of the solution is used in the test, or 1·6 parts per 1,000,000. This sensibility was in close agreement with the error in weighing of the work under way, and would therefore have been satisfactory had it not been found that the reagent must practically be made fresh on the day it is used or the results are not dependable. The reagent decreases in sensitiveness. After six days' standing in a stoppered bottle, in one case, the reagent failed to detect any copper in an N/5000 solution. One week later copper could scarcely be detected in an N/1000 solution, with the original reagent. The addition of ammonium hydroxide to reduce the yellow colour assumed by the deteriorated ammonium sulphide reagent did not seem to improve its sensibility. The work on ferrocyanide resulted so satisfactorily that the ammonium sulphide deterioration was not further investigated.

Potassium Ferrocyanide Reagent.—This reagent gave the best satisfaction. It is in quite common use, but is frequently erroneously thought to be entirely too delicate. It was prepared by dissolving 1 grm. of Baker's chemically pure ferrocyanide in 50 cc. of water. This was amply strong to precipitate the copper, and not so coloured as to interfere greatly with the delicacy of the test. A pinkish brown colour was obtained with the dilutions of copper salt used. Three drops of the reagent were used, and the tests conducted as described above. The copper in N/20,000 solution could easily be detected by this reagent, but the colour difference became less and less marked as dilution took place. At a dilution of N/35,000 the colour difference (compared with the blank) was just discernible. This was therefore the limiting sensibility, and indicates the presence of 0·00009 grm. of copper in 100 cc. when 1 cc. is used in the test, or 0·91 part per 1,000,000. This is not quite twice as delicate as the test with fresh ammonium sulphide. It is much more delicate than when the test is performed with a drop of the solution on white porcelain, even when the ferrocyanide is as dilute as 0·1 per cent.

Influence of Reagents.—The influence of the proportions of the reagent and its auxiliaries as well as other substances was studied in the case of potassium ferrocyanide by means of Nessler tubes in 50 cc. portions. The tubes were wrapped with black paper. Difficulty was at first experienced in using the ferrocyanide test on samples from a nitric acid electrolyte. This was caused by a yellowish-green coloration which formed in the tube containing the electrolyte, masking any pink colour which be produced. Sometimes the pink which appeared was at once superseded by the green colour. The interfering colour did not seem to appear in samples containing a negligible amount of copper (0·1 mgrm. or less in 125 cc.). The addition of 2 per cent of nitric acid to the ferrocyanide-copper nitrate mixture produced cloudiness, interfering with the delicacy of the test. Acetic acid, on the other hand, did not interfere, and really produced a better coloration. Ammonium hydroxide seemed to destroy the copper ferrocyanide colour, and gave a colourless to a green colour when in excess. The addition of an acid brought this colour out again. An excess of potassium ferrocyanide affects the delicacy of the test in that it changes from pink to yellow, thereby slightly decreasing the delicacy. Ammonium nitrate increases the delicacy of the test. Excess of acetic acid is of little influence. Ammonium acetate has no effect.

Interference of other Metals.—Zinc has no effect on the

delicacy of the ammonium hydroxide reagent when sufficient excess is added and time allowed to re dissolve the hydroxide first precipitated. This is true even when a very great excess of zinc is present, such as would obtain when 10, 20, 30, and 40 per cent alloys of zinc with copper in 1 grm. quantities were dissolved in 100 cc. and the copper reduced in amount until it was N/3000. These are the practical conditions met with in the electrolytic separation of copper from zinc.

N/35,000 copper solutions containing the excess in amounts of zinc just mentioned gave very unsatisfactory results with ferrocyanide, however, because of the precipitation of zinc ferrocyanide. This reagent was therefore useless in the presence of zinc.

Conclusions.—I. The contradictory state of the literature indicates that results in colorimetric examinations are not comparable unless the volumes worked with and the diameter of the apparatus used are at least approximately known.

II. It has been found with the method used that the end-point of an electrolytic precipitation of copper, no other metals being present, may be detected by—

Ammonium hydroxide with an error not greater than 0·105 per cent;

Ammonium sulphide with an error not greater than 0·015 per cent;

Potassium ferrocyanide with an error not greater than 0·009 per cent;

provided the volume of the electrolyte was 100 cc., and there was originally present 1 grm. of copper.

III. The recommended procedure for the detection of traces of copper at the end of electrolytic copper precipitation in the kinds of solutions indicated, is as follows:—Take 1 cc. of the sample in a narrow test-tube constructed as described. Make alkaline with ammonium hydroxide, acidify with glacial acetic acid, and add 2 drops of 2 per cent $K_4Fe(CN)_6$ solution. A pronounced red colour indicates more than 1 mgrm. of copper. Make similar additions to another tube as a blank, replacing the sample to be tested by distilled water. If by comparison the tubes are practically of the same colour, then there is present not more than 0·1 mgrm. of copper in 100 cc. of the solution.

NATIONALISATION OF SOURCES OF RADIUM IN UNITED STATES.

Report of Committee on Mines and Mining.

The Committee appointed to consider the question of securing an adequate supply of radium for the use of the Government and people of the United States began on January 19, 1914, to hold public hearings for the purpose of obtaining information on the subject from those in favour as well as from those opposed. The Committee gave six days to the hearings, and gave full opportunity for those interested to appear and testify. As a result of these hearings the Committee recommended that a Bill be passed to provide for and encourage the prospecting, mining, and treatment of radium-bearing ores in lands belonging to the United States, for the purpose of securing an adequate supply of radium for Government and other hospitals in the United States, and for other purposes. This Bill gives to the General Government a preferential right to purchase the radium-bearing ores from lands now owned by the Government, at such prices to be fixed by the Secretary of the Interior as will cover the cost of and encourage mining operations, and under conditions that require the full and prompt development of the radium deposits for the benefit of the people. At the same time it furnishes to the actual prospector or miner a steady market for his ores and sure and prompt payment for the material when sold—two conditions that he has not always enjoyed in the past. The Bill safeguards the interests of all the people, and provides against unforeseen conditions by authorising the Secretary of the Interior to fix semi-annually the price to be paid for the ores under conditions that will insure the prospecting for and mining of them; allows the Secretary to permit the sale and delivery of these ores after or without tender to the United States, if conditions arise which make this advisable, *i.e.*, if conditions arise under which the Government is for a time unprepared to purchase the ores; and it permits him to accept or purchase radium-bearing ores from deposits already in the hands of private individuals, should such tenders be made and the material be needed. It also authorises him to dispose of the radium extracted under conditions that will best serve the needs of the people of the United States, keeping in mind always the needs of the many who are unable to bear the burden of expensive journeys or costly treatment which now limit such treatment to the few. It authorises an appropriation to cover the cost of the mining of the radium-bearing ores on the public lands and the extraction of the radium. If such policy is deemed wise the Secretary of the Interior may sell a part or all of the radium produced to American hospitals at cost of production and turn the receipts therefrom into the Treasury, thus reimbursing the Government in part or in full for the expenditures under this act.

From information brought before it the Committee is convinced of the great public need of the legislation herein proposed. It has been shown by the highest medical authority and to the Committee's satisfaction that radium is a cure for certain forms of cancer, particularly those of an external nature which have not progressed beyond the reach of this or any other remedy; that it is almost a specific in certain forms of giant sarcoma; and that many cases of cancer quite beyond the hope of surgery can be and have been cured by this agent. From the evidence at hand it seems probable that by the use of larger quantities of radium than are now available, a large number of present failures might be transformed into cures. Unfortunately up to the present time no American surgeon has been able to procure for use in any case more than 1 grm. of radium, and the total quantity now available for all American hospitals does not exceed 2 grms.

As there are estimated to be over 200,000 cases of cancer in the United States, and 75,000 people yearly are said to die of cancer, the importance of this discovery and the seriousness of this situation for the American people cannot be over estimated. It has been shown to the satisfaction of the Committee that during the last two or three years the United States has supplied from two to three times as much of the raw material used in producing radium as all the rest of the world together; that this material has for the main part been exported to foreign countries at prices entirely incommensurate with the actual value of the contained radium; that up to January 1, 1914, only 2 grms. of this material had been produced in the United States; and that one company—the only company in the United States now actually producing and selling this material—has already contracted abroad for the major part of its 1914 output. It has also been shown that on account of the great foreign demand for the material it is practically impossible to procure radium at any price for immediate delivery, and that when future deliveries are promised the price is so high and so far beyond the actual cost of production that there is small hope that this remedy will become generally available for rich and poor alike in the United States.

The Committee is therefore convinced that Congress should immediately take steps, as proposed in this bill, to develop the radium resources still belonging to the people of the country, and to do this under conditions that will secure and make immediately and widely available the largest possible supply of this radium for the treatment of the sufferers from cancer among the people of the United States. The Bill now reported will accomplish this purpose in a manner which, it is believed, instead of discouraging will encourage and stimulate the prospector to discover and mine the radium ore deposits by giving him a certain and fair reward for his discovery and his work.

Resources.

Radium ores are known to occur in several localities, but always in comparatively small amounts. The richest radium-bearing region is undoubtedly the Paradox Valley region in Montrose County, Colo., where the ore is carnotite, containing uranium and vanadium besides radium. Mines at Joachimsthal, Austria, have been taken over by the Austrian Government, and are being developed through governmental resources. The only ore there is pitchblende, an impure oxide of uranium carrying radium. Pitchblende is also found in Gilpin County, Colo., whence several tons of ore have been shipped abroad to contribute a little to the radium supply.

In the old tin-mining district in Cornwall, England, some pitchblende is also found, and an English company and one of the French companies are reputed to get their chief supplies from low-grade ores on the dumps and in the stopes of the old tin mines.

Deposits of autunite, another radium-bearing mineral, are known to occur in Portugal and also in Australia, and a few hundred milligrms. of radium are yearly produced from these ores. Carnotite is, however, the chief source of radium at present. Very low-grade deposits of carnotite mixed with another mineral (ilmenite) are known to occur in Australia, and a plant has been started in that country which is producing from 100 to 200 mgrms. of radium per month. A deposit has also been found at Ferghana, Russian Turkestan. It has not yet become a regular source of supply, and there is no reason to believe, from any report issued up to the present time, that it will prove a large source of radium. In fact, no deposit of radium ores anywhere discovered gives any promise of supplying material enough to meet the immediate demands.

The carnotite deposits of Colorado and Utah are, as before stated, the most extensive in the world. They have, however, been very wastefully exploited, some 4 tons more or less of low-grade ore having been thrown on the dumps or mixed with mine waste for every ton of shipable ore so far marketed.

Present Ore Supplies.

According to the testimony presented to the Committee from 700 to 1000 claims have been at one time or another staked in Colorado and Utah; of these claims perhaps 300 may eventually be worked and 150 may be considered reasonably good. These claims have been for the main part bought up by a few interests, and for only a few claims has the prospector obtained more than 50 dols. to 200 dols. a claim. The Standard Chemical Co., of Pittsburgh, controls approximately 170 of these claims; the General Vanadium Co., of Liverpool, England, 58; the Radium Co., of America, 20 to 25; Thomas F. Curran, 70 or more; O. B. Wilmarth, 20 to 25; and the National Radium Institute, 16. The others are scattered among the smaller producers. Many claims are being located at present, and if a supply of radium is to be preserved for America prompt action by Congress is necessary.

Future Ore Supplies.

As to future ore supplies no definite statements can be made, the testimony presented to the Committee being contradictory. Those who now own claims are very sure that other supplies will be found in quantity. There is no reason to believe that further discoveries will not be made, although the mining engineers reporting to the Denver Chamber of Commerce, the employees of the Bureau of Mines, and members of the Geological Survey state that all known deposits are already located. Accordingly it will probably be necessary, if the Government is to secure immediate supplies, to purchase from owners of claims already located, as well as to put forth every effort to open up new deposits.

The carnotite region is known to be extensive, there being an area of something over 480,000 acres within which pockets of carnotite are apt to occur. But in many places the carnotite-bearing stratum has been eroded away, and in many others it is so deeply buried by later beds that there is no reasonable hope of ever obtaining the supplies that are undoubtedly embedded therein. There are, however, certain areas where this stratum is only a few feet under the surface, as well as many places on the canyon sides where it outcrops and where pockets of carnotite are likely to be found. These carnotite deposits, however, are mainly small, no claim having yet produced without exhaustion more than 500 tons of shipable ore. Most of the pockets contain less than 50 tons. These pockets are not connected by stringers, and there is no evidence of vein formation. Accordingly the finding of one pocket is no indication that others are adjacent, although sometimes this may be the case. With the large number of prospectors now in the field it is hoped and expected that new discoveries will be made, and that sufficient bodies of ore will be opened up to assure the radium necessary for American hospitals.

Saving of Waste.

Many of the claims already worked have on their dumps considerable quantities of ore that is too poor to ship at such prices as have prevailed in the past. There is every reason to believe, however, that concentration methods can be developed by which much of this ore can be concentrated on a basis that will make a large part of it available for use. This is a very important work for the Government to do, as more than twice as much radium has been wasted as has actually found its way to market. Certainly every effort should be made to conserve this almost priceless material.

United States Production and Exportation.

As in most radium ores there is a fairly definite ratio of radium to uranium (1 to 3,000,000), the amount of radium obtained and exported can be roughly calculated from the uranium content of the ores sold. According to the figures of the Bureau of Mines, carnotite ores carrying 28·8 tons of uranium oxide were produced in 1912, and practically the entire amount was exported. In that year the uranium content of the major part ran between 2 and 3 per cent of uranium oxide, as, owing to the cost of transportation, no ore carrying less than 2 per cent could be marketed. From the ores shipped abroad in 1912, 11·43 grms. of anhydrous radium bromide could have been and probably were extracted. In 1913, according to preliminary figures of the United States Geological Survey, 2140 tons of ore were produced, of which 1198 tons were shipped to works in this country and 942 tons were exported. However, owing to the cost of transportation only the richer ores were exported, so that radium equivalent to about 7·5 grms. of anhydrous radium bromide, more than one-half of the total American production for the year, was sent abroad. One foreign company did not work its plant in the Paradox Valley, Colo., during the greater part of the year, because it was building a new plant in Liverpool, and it cost less to leave the ore in the mine than to take out the ore and store it in England. This company will be a large exporter of carnotite from Colorado and Utah during 1914.

It is improbable that all of the ores exported are now represented by finished product, but the actual production for 1912 and 1913 cannot be much less than the quantity mentioned. The total quantity of uranium exported in 1911 was almost equal to that exported in 1912, and ores are still being sold for treatment abroad. There can be no doubt that in 1912 and 1913 there was obtained from American ores more than twice and probably three times as much radium as from all other sources combined.

The carnotite prospects and mines of the West have been described in *Bulletin* 70 of the Bureau of Mines, and the subject is further treated in "Advance Chapters from Mineral Resources for 1912," by F. L. Hess, of the United States Geological Survey. The mines are for the main part in Montrose and San Miguel Counties, Colo., and in a somewhat more extensive territory just to the west and north-west of these deposits in Utah. Since *Bulletin* 70

was written, prospecting in this region has been extensive. Many agents of foreign manufacturers have been in the country seeking supplies for shipment abroad, and a much stronger demand for ores has caused prices to advance, so that at present ore containing 2 per cent of uranium oxide readily brings 80 dols. per ton at the railroad at Placeville, Col. Correspondingly higher prices are obtained abroad, and some private producers who were able to contract for considerable quantities report even higher prices.

Owing to the interest aroused and to the proposed withdrawal of radium-bearing lands there has been a decided increase in prospecting, and some important new finds have been made. Although many claims have been staked in different parts of the radium-bearing region, the most important finds have been at the summit of Big Canyon at the head of Lisbon Valley, Utah, just across the State line from the McIntyre district, Colorado. Other important finds are reported in the Henry Mountains, about 100 miles south-east of Green River, and in a district about 7 miles north-east of Monticello, Utah. Development work has been carried on at Gateway and also in the western part of the Paradox Valley, the original scene of the main operations.

(To be continued).

THE SCIENTIFIC WEEK.

(From Our Own Paris Correspondent).

A Fossil Gas a Hundred Millions of Years Old.

The question of the presence in the atmosphere and of the origin of the five rare gases at present known—helium, neon, argon, krypton, and xenon—is one of the most interesting features of modern science. In particular, helium, which exists in all hot springs and results from the disintegration of the radioactive substances in the bowels of the earth, contributes in keeping up the radioactivity of the atmosphere by the permanent emission of penetrating atoms, electrified, moved by a prodigious speed, and capable of playing an important though still imprecised rôle in the functional acts of life. Prof. Moureu, in collaboration with M. Lepape, has just informed the Academy of Sciences that coal damp constantly contains, in company with other rare gases, enormous proportions of helium. It is thus that the mine of Frankenholz, in Westphalia, pours out into the atmosphere as much as 4000 cubic metres of helium a year. However, coal possesses only very small quantities of radium and thorium incapable of explaining the production of so much helium. It is thus certain, in these conditions, that the abundant helium of coal-damp is, for the far greater part, fossil helium, dating from the carboniferous period, which enables its age to be reckoned at from 50 to 100 millions of years!

The First Thesis for the Doctor's Degree in Pedological Science.

This title has just been conferred for the first time by the International Faculty of Pedology of Brussels, 69, rue de la Culture, directed by the lady doctor J. Toteyko. This faculty has grouped together all the disciplines concerning the scientific knowledge of children, without forgetting the practical applications of Pedagogy, and it has raised pedology to the dignity of a real science able to fill the programme of a university course of teaching. Considered from this point of view, the crowning of the pedological studies necessarily includes the accomplishment of an original work; that is to say, the composition of a thesis for the doctor's degree. The first to receive this degree is Mdme. Lifoka-Librach, who after three years' experimental study pursued in the school of Brussels on 420 school children, has succeeded in drawing up a work of more than 120 pages, entitled, "On the Relations between Sensorial Acuity and the Development of the Intelligence." Mdme. Librach has managed to obtain a very strict correlation between the intelligence of children and the fineness of their senses. It is a truth of a statistical order. The relation sought for appears more distinct for young children of nine or ten years than for those who are nearing the end of their primary studies. The work contains a great number of applications specially interesting for pedagogy.

Lighting by Neon Tubes.

Neon is one of the five rare gases contained in the atmosphere. Its applications for lighting purposes are very curious. Prof. d'Arsonval has presented before the Academy a work of M. George Claude, showing that large neon tubes are not superior to small ones, for the production of light in these tubes depends on the product of the volts by the ampères, that is to say, on the force expended. On the contrary, the luminous production remains excellent, and of the rank of half a watt per candle, down to very small diameters, 10 mm. and less. It becomes then easy to make very short tubes, exceedingly easy to manipulate, giving a very weak luminous force, with an excellent production, which had been impossible up till now for lighting by luminescence.

How Oceans are Formed.

M. Fermier has presented a paper by M. Emile Belot on the "Physical Laws of the Formation of Primitive Oceans and Continents." On the Earth and on Mars oceans dominate greatly in the austral hemisphere. This fact may be attributed to the translation in the south-northerly direction of these planets in the primitive nebula. The friction of this nebula on the exterior surface of the planetary atmosphere determines a north-southerly circulation, which is completed on the surface of the condensed nucleus by a south-northerly circulation. It is then around the antarctic that cold vertical currents can reach the nucleus and that the temperature can at first be inferior to 364° (the critical temperature of water). The condensation of the oceans is then produced around the South Pole, determining currents towards the Equator, which explain the formation into a point, towards the south, of the austral continents. The calculation, founded on the permanent regime of the speeds of these currents and of the solid matter that they transport, is verified by direct measures—thus, below sea-level 2000 metres the breadth of the oceans is constant on the parallels of the austral hemisphere, and the breadth of the continents is constant on the parallels of the boreal hemisphere.

New Method of Analysing Drinking Water.

Prof. Moureu has shown, according to M. Halmejac, of Bordeaux, that the richness of waters in chlorides is proportional not only to the organic matters but to the microbian germs that these waters contain. Whence is to be derived the possibility of appreciating, by a simple determination of the chlorides, whether a water is fit for drinking or not.

The Signs of Fatigue.

With a view of determining the methods of scientifically regulating labour and work, M. J. M. Lahy, in a paper presented by M. Edmond Perrier, director of the Paris Natural History Museum, has fixed the means of recognising the objective signs of fatigue in the so-called modern professions which do not require great muscular effort. Experiments carried out by him in 1903 on the postmen employed in the railway postal vans, on printers, linotypists, and type writers, have given concording results. The signs of fatigue in these workers are constituted by an increase of the pressure of the blood and by a slackening of the time of reaction.

The Transmission of Hertzian Waves.

MM. Prosper and Rothi have sought to verify the variations of the transmission of the Hertzian waves according to the state of the atmosphere. Prof. Bouty,

who has informed the Academy of their studies, confirms the preceding researches. The transmission of the waves of Hertz takes place better in the night than in the day.

THE ALTERATION OF SPEECH BY MICROPHONES.

For some time past there have been attempts made to utilise the oscillographic study of microphonic currents to analyse the sounds of the voice and to improve telephonic transmission. But the diagrams thus taken off by different experimenters, and which were thought to be comparable, at least as far as the transcription of vowels was concerned, have now been recognised as discordant. This fact has led M. A. Blondel and M. Polak to take the question up again, following a method which utilised the Blondel oscillography. They explain this method in the *Annales des Postes, Telegraphes, et Telephones* of December last. It appears from this that microphones can introduce their own oscillations, which are of independent frequency to that of the voice, when their membranes or granules of carbon are not deadened or slackened. But, on the other hand, an excess of padding or deadening may stifle certain sounds. The granulated microphones give many parasitical vibrations. The authors have merely enregistered diagrams of vowels, without going into the study of consonants, which are still more complex and more liable to deformation.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, March 5, 1914.

Sir WILLIAM CROOKES, O.M., President, in the Chair.

Papers were read as follows:—

"*Action of Light on Chlorophyll.*" By HAROLD WAGER, F.R.S.

When chlorophyll is decomposed by light, at least two distinct substances are formed, one of which in an aldehyde or mixture of aldehydes and the other an active oxidising agent, capable of bringing about the liberation of iodine from potassium iodide. This can be demonstrated in various ways.

The decomposition of chlorophyll appears to be due directly to the action of light and is not an after effect of the photo-synthesis of carbon dioxide and water. It takes place only in the presence of oxygen, and it appears to be a case of photo-oxidation, for oxygen is used up so completely in the process that chlorophyll can be used instead of pyrogallol and caustic potash to determine the amount of oxygen in a given amount of air. In the absence of oxygen no bleaching takes place. Carbon dioxide is not necessary to the photo-decomposition of chlorophyll and is not used up in the process, even when present in considerable quantities. The bleaching of chlorophyll takes place just as rapidly and completely in its absence as in its presence, and the same two substances are produced. Formaldehyde appears to be formed in small quantities, but the main bulk of the aldehyde produced by the photo-decomposition of chlorophyll is not formaldehyde. The oxidising substance does not give the reactions for hydrogen peroxide; it is possibly an organic peroxide.

The decomposition of chlorophyll and the production of aldehyde is also brought about by the action of oxidising agents such as hydrogen peroxide and permanganate of potash. This may take place in the dark very rapidly in the case of permanganate of potash, but very slowly in the case of hydrogen peroxide. In the light the oxidation due to hydrogen peroxide is, however, much accelerated.

The bleaching of chlorophyll *in situ* in green leaves gives the same products as the chlorophyll extracts outside the plant.

"*Formaldehyde as an Oxidation Product of Chlorophyll Extracts.*" By C. H. WARNER.

"*Controlling Influence of Carbon Dioxide in the Maturation, Dormancy, and Germination of Seeds.*" By FRANKLIN KIDD.

Experiments are described showing that germination of seeds can be completely inhibited by carbon dioxide in the atmosphere (20—30 per cent, varying with the temperatures used). This inhibition is not accompanied by injury. The seeds germinate at once after removal from inhibitory CO_2 pressures.

In one case (*Brassica alba*) a still more striking result is obtained. Inhibition is not terminated by removal of the seeds from the CO_2 pressures to air, but continues indefinitely, though the seeds lie in well aerated and moist conditions, at 15°—20° C. This condition of continued dormancy in the face of a favourable environment for germination is at once suggestive of cases of "delayed germination" often met with in nature, where seeds do not germinate but lie indefinitely in soil in apparently good germinating conditions.

This continued inhibition of *Brassica* seeds when removed from atmospheres containing CO_2 to air is found to be terminated by removal of the testas, or by complete drying and re-wetting of the seeds.

The conclusion indicated is that a change in the testa rendering it less permeable to gases is produced by the action of CO_2, whereby after removal of the seeds to air the CO_2 produced in the embryo will be to an increased degree held up in the tissue, while at the same time the amount of oxygen penetrating the testa from the atmosphere will be lowered. The seed is thus sealed by its testa for a long period of dormancy under the influence of carbon dioxide.

Experiments in the field showed that this action of CO_2 may actually occur in nature. If a quantity of green plant material is buried deep in the ground, seeds planted in the soil over this decaying material are inhibited in their germination by the CO_2 produced beneath them. This is of agricultural significance, and the fact that in the case of mustard seeds suspension of vitality continues even after the external CO_2 has been removed, suggests an explanation of the common occurrence of dormant seeds of this plant in fields, and possibly of other natural cases of delayed germination.

"*Functional Correlation between the Ovaries, Uterus, and Mammary Glands in the Rabbit; with Observations on the Œstrous Cycle.*" By J. HAMMOND and F. H. A. MARSHALL.

"*The Chromaffine Systems of Annelids and the Relation of this System to the Contractile Vascular System in the Leech, Hirudo medicinalis.*" By J. F. GASKELL, M.D.

CHEMICAL SOCIETY.

Ordinary Meeting, March 5, 1914.

Prof. W. H. PERKIN, LL.D., F.R.S., President, in the Chair.

MESSRS. E. E. Turner, John K. Wood, A. Bramley, Bertram Campbell, and Ivan R. Gibbs were formally admitted Fellows of the Chemical Society.

The names of the Fellows recommended by the Council for election as official and ordinary Members of Council, 1914—1915, were read from the Chair.

The PRESIDENT announced that the Rooms of the Society will be open for an informal meeting of the Fellows on Thursday, April 30th, from 8 to 10 p.m. Smoking will be permitted, and light refreshments will be provided. Fellows are invited to exhibit apparatus and specimens of interest, and to show experiments, and those wishing to do so are requested to communicate with the Honorary Secretaries not later than the Monday previous to the meeting.

It was also stated that a meeting of the Faraday Society will be held in the Rooms of the Chemical Society on Friday, March 27th, 1914, when a general discussion on "Optical Rotatory Power" will take place. Fellows of the Chemical Society are invited to attend. The meeting will be held from 5 to 6.30 p.m., and from 8 to 9.30 p.m., tea being served at 4.30. Further particulars can be obtained from the Secretary of the Faraday Society, 82, Victoria Street, S.W.

Certificates were read for the first time in favour of Messrs. Raymond Foss Bacon, B.Sc., Ph.D., Mellon Institute of Industrial Research, University, Pittsburg, Pa., U.S.A.; Robert Reginald Baxter, B.A., St. John's College, Oxford; Brojendranath Ghosh, M.Sc., 59, Hereford Road, Bayswater, W.; Richard Selwyn Haskew, Cwmbran, Newport, Mon.; Ralph Waldo Emerson MacIvor, 47, Victoria Street, Westminster, S.W.; Henry Ratcliffe, 38, Sefton Terrace, Beeston Hill, Leeds; John Rogers, 195, West George Street, Glasgow; Percy Charles Rundell, Glenthorne, St. Albans Crescent, Woodford Green; Max Herbert Tagg, B.Sc., Brentor, Clayton Avenue, Wembley; Albert Watkins Maggs Wintle, Holly House, Saltcoats, Ayrshire.

Of the following papers those marked * were read:—

*59. "*The Atomic Weight of Vanadium.*" By Henry Vincent Aird Briscoe and Harry Frank Victor Little.

The ratios $VOCl_3 : 3Ag$ and $VOCl_3 : 3AgCl$ have been re-determined. Vanadyl trichloride was decomposed by aqueous ammonia, acidified with nitric acid, and the chloride either titrated against silver according to the method of Richards and Wells (*Journ. Am. Chem. Soc.*, 1905, xxvii., 459), using a modified nephelometer to determine the end-point, or precipitated as silver chloride and weighed. A new type of apparatus, designed for fractional distillation in a vacuum with the complete exclusion of moisture, was used for the distillation of the vanadyl trichloride and its collection in glass bulbs, and the trichloride was weighed in a manner which obviated the necessity for collecting fragments of broken bulbs.

The results obtained are as follows (Ag = 107·88; Cl = 35·457):—

9 expts. : $VOCl_3 : 3Ag = 0{\cdot}53554 \pm 0{\cdot}000008$, whence V = 50·950.

2 expts. : $VOCl_3 : 3AgCl = 0{\cdot}40307$, whence V = 50·952.

For a number of reasons these results may be slightly too low, and the rounded-off value V = 50·96 is preferred. This result is in very close agreement with that deduced by McAdam (*Journ. Am. Chem. Soc.*, 1910, xxxii., 1603) from measurements of the ratio $NaVO_3 : NaCl$.

Discussion.

In reply to the President, Mr. Little stated that part of the oxide of vanadium which formed the starting material had been formerly used by Sir Henry Roscoe in his researches on vanadium. A small amount of arsenic present in another portion of the oxide was incidentally eliminated when converting the oxide into vanadyl trichloride, but otherwise no initial purification of the oxide was attempted. The vanadyl trichloride, however, was fractionated until a preparation was obtained quite free from phosphorus and arsenic, and having a constant boiling-point (127°). The subsequent fractionation of this product was effected in a vacuum, and no further boiling-point observations were made.

*60. "*The Isomerism of the Oximes. Part III. The Hydroxybenzaldoximes.*" By Oscar Lisle Brady and Frederick Percy Dunn.

The authors have investigated the hydroxybenzaldoximes, but have failed to obtain stereoisomerides or any confirmation of the existence of the supposed isomeric *m*-hydroxybenzaldoxime described by Jowett (*Trans.*, 1902, lxxxi., 707). Dollfus (*Ber.*, 1892, xxv., 1924) assumed that in the monoacetyl derivatives of these oximes the oximino-group was acetylated, but the authors have been able to show that in the case of *p*-hydroxybenzaldoxime it is the phenolic hydroxyl that is acetylated, and not the oximino-group, the compound thus being *p*-acetoxybenzaldoxime. This and the parent hydroxy-oxime have been proved to possess the *anti*-configuration, and the stereoisomeric *p*-acetoxybenz*syn*aldoxime has been prepared.

In the case of the acetyl derivative of salicylaldoxime, however, it has been shown that the oximino-group is acetylated.

Discussion.

Dr. Pyman pointed out that Dr. Jowett laid no claim to the discovery of a stereoisomeric *m*-hydroxybenzaldoxime. The oxime had been prepared from *m*-hydroxybenzaldehyde amongst half-a-dozen other derivatives for the purpose of identification, and the discrepancy of melting-point was noted, but not fully investigated.

In reply to the President, Mr. Brady stated that it would probably be difficult to obtain stereoisomeric oximes from 4 : 5-methylene-*o*-tolualdehyde on account of the methyl group being in the ortho-position with respect to the oximino-group; with reference to the methoxybenzaldoximes, the two isomeric *p*-methoxybenzaldoximes had been obtained, but the ortho-compound existed only in one form; the meta-compound had not been investigated.

In reply to Dr. Pyman, he said that there was no wish on the part of the authors to suggest that Dr. Jowett claimed to have obtained an isomeric *m*-hydroxybenzaldoxime; they were, however, of the opinion that it was impossible to obtain a compound melting at 138° by recrystallising *m*-hydroxybenzaldoxime from benzene.

*61. "*The Constituents of the Leaves and Stems of Daviesia latifolia.*" By Frederick Belding Power and Arthur Henry Salway.

Daviesia latifolia, R. Br. (Nat. Ord. *Leguminosæ*), is a shrub indigenous to Victoria, Australia, where, on account of the bitter taste of the leaves, it is known as the "Native Hop Bush."

An examination of freshly collected material, consisting of the leaves and stems of the above-mentioned plant, has shown that its bitterness is due to a crystalline benzoyl derivative of a new disaccharide, the latter (*glucoxylose*) yielding on hydrolysis 1 molecule of dextrose and 1 molecule of xylose. The bitter compound possesses the empirical formula $C_{25}H_{28}O_{12},H_2O$, melts at 147—148°, and has been designated *dibenzoylglucoxylose*.

Besides a small amount of an aromatic essential oil, the following additional constitnents of the plant have been isolated or identified:—Benzoic, salicylic, *p*-coumaric, and fumaric acids, and a mixture of fatty acids, consisting of palmitic, stearic, and linolic acids; a quercetin glucoside, $C_{27}H_{30}O_{16}$, which is probably identical with rutin; myricyl alcohol; hentriacontane; a phytosterol, $C_{27}H_{46}O$; and a sugar which yielded *d*-phenylglucosazone (m. p. 210°). The resinous material, from which some of the above-mentioned substances were obtained, amounted to about 8·6 per cent of the weight of drug employed.

Discussion.

Dr. Power, in reply to a question by the President, stated that the recent chemical examination of hops had revealed the presence of no substance similar in character to the bitter principle of *Daviesia* leaves. It was also noted that no botanical relationship exists between the leguminous shrub, *Daviesia latifolia*, R. Br., and the common hop plant, *Humulus Lupulus*, L.

In reply to a question by Mr. Baker, it was explained that the new disaccharide, *glucoxylose*, had only been directly isolated in the form of its crystalline benzoyl derivative, *dibenzoylglucoxylose*. The amount of the latter compound present in the leaves appeared to be somewhat less than 1 per cent.

*62. "*The Composition of some Mediæval Wax Seals.*" By James Johnston Dobbie and John Jacob Fox.

An account was given of the examination of the com-

position of a number of mediæval seals, ranging in date from the thirteenth to the beginning of the sixteenth century.

The seals were found to consist of beeswax alone, or of beeswax mixed with resin in various proportions. The resin could not be identified except in two cases, in which it gave the reactions for colophony.

The red seals were coloured with vermilion, the green with verdigris, the brown and black with verdigris and organic matter.

The beeswax which formed the sole constituent of an impression of the Great Seal of 1350 was practically unaltered in chemical and physical properties, except as regards its power of absorbing iodine, which was slightly less than that which beeswax usually exhibits.

63. "*Experiments on the Rate of Nitrification.*" By RICHARD MOORE BEESLEY.

Solutions of nitrogenous substances were inoculated with a mixed culture of nitrifying and hydrolytic organisms, which were obtained from a secondary contact bed, and the nitrification was allowed to proceed under strictly comparative conditions, with the object of determining the comparative rate of nitrification.

The following substances were employed:—Carbamide, thiocarbamide, uric acid, asparagine, glycine, acetamide, methylamine sulphate, aniline sulphate, ammonium oxalate, and ammonium sulphate. The solutions, with which were incorporated suitable mineral media, were made of such a strength as to contain 100 milligrms. of nitrogen per 500 cc.

The course of the nitrification was followed through by means of periodic determinations of the ammoniacal, nitrous, and nitric nitrogen figures. Under these conditions it was found that the various substances nitrified at approximately the same rate, with the exception of thiocarbamide and aniline sulphate, which completely failed to nitrify. Evidence has also been obtained to the effect that in the bacterial oxidation of nitrogen, compounds intermediate between ammonia and nitrous acid are formed.

64. "*Studies of the Constitution of Soap Solutions. The Alkalinity and Degree of Hydrolysis of Soap Solutions.*" By JAMES WILLIAM MCBAIN and HERBERT ERNEST MARTIN.

From electromotive force determinations, the dissociation product of water at 90° is calculated to be $69 \cdot 7 \times 10^{-14}$; this result is chiefly of interest in discussing the high real temperature-coefficient of the hydrogen electrode, which is ignored by recent convention.

The hydrolysis and true alkalinity of soap solutions has been quantitatively determined for the first time. In concentrated solutions hydrolysis amounts to only a fraction of a per cent, and even in 0·01/N sodium or potassium palmitate it only amounts to 6·6 per cent, and thus the high conductivity of soap solutions is definitely shown not to be due to free alkali. The novel suggestion was advanced that it may be due to highly charged aggregates or micelles exhibiting even an equivalent conductivity comparable with that of ordinary ions (see McBain, *Trans. Faraday Soc.*, 1913, ix., 99; *Kolloid. Zeitsch.*, 1913, xii., 256). This suggestion, if confirmed, may apply to such diverse cases as protein salts, dyes, and certain non-aqueous solutions.

In the presence of even one equivalent of free palmitic acid soap solutions are still appreciably alkaline. On the other hand, the alkalinity of solutions containing an excess of alkali is practically that of the added alkali. There is thus no measurable sorption or formation of basic soap in the presence of 0·1/N alkali.

Sodium chloride at first decreases, but in larger amounts again increases, the alkalinity of soaps, in accordance with the suggested rule that any influence tending towards coagulation increases the alkalinity of these solutions.

(To be continued).

INSTITUTE OF CHEMISTRY.

Annual General Meeting, March 2, 1914.

Prof. RAPHAEL MELDOLA, President, in the Chair.

THE annual accounts were received on the motion of Mr. A. GORDON SALAMON, the Hon. Treasurer, seconded by Prof. J. MILLAR THOMSON.

The Treasurer's remarks indicated that during the twenty-one years tenancy of its present premises the Institute had been able to make its income suffice for maintenance and steady development, but with the move to the new buildings, which would take place during the present year, the Council would have to look carefully to its resources. Any anxiety on that account would be relieved considerably by the realisation of their hope that the amount of the total expenditure on the new buildings would be subscribed by the end of the year. The response to the appeal to the Buildings Fund was somewhat remarkable in that about £17,000 had been collected at a cost of less than £250. Probably £1000—possibly less—would make the position of the Institute in this respect quite sound, and enable the Architect and Buildings Committee to effect considerable improvements in the finish and equipment of the building.

The Report of the Council having been received and adopted, the meeting proceeded to elect Censors and Auditors.

The PRESIDENT, in the course of his Address to the Fellows and Associates, referred to the progress of the Fund for the new buildings of the Institute, and acknowledged the generous support of many companies, firms, and individuals, other than members, who had contributed. Taking into account the promise of an anonymous benefactor to double every subscription received beyond £12,000 up to the amount of £2500, it was probable that less than £1000 was now required; but if more were received the Buildings Committee could easily invest it in improved and more serviceable finishings. The building had progressed most favourably until the trades dispute, and, as there were signs of approaching settlement, it was hoped that the work would be completed before the autumn.

Referring to the endeavours of the Institute to secure fuller recognition for the profession of chemistry, the President recalled the evidence given by Sir William Tilden and Sir William Ramsay, as representatives of the Institute, before the Royal Commission on the Civil Service. The main portion of their evidence related to the conditions of service of chemists engaged in the Department of the Chief Inspector at Woolwich Arsenal. The Council of the Institute, in the Memorandum submitted to the Royal Commission, stated that the chemical staff in that Department should be controlled by a chemist of the highest efficiency. The rapid development of science in every direction was leading to increased specialisation. The real expert, whose knowledge and experience were of most value to the community, was the highly trained man who had specialised in some particular field. Surely such a man was the most competent to control the work of any public department which was concerned with his own subject. The training and experience which had raised him to his position of efficiency were no less protracted and severe than those required for the attainment of similar status in any other profession. Why, therefore, should there be this tendency to subordinate expert scientific service to non-expert control? The question of national defence was an important one, and the valuation and control of materials required in our arsenals, and the study and application of new discoveries having any bearing upon "the arts of war," were no less matters for chemical control than the conduct of an army in the field would be a matter for control by the General Staff. Yet, while the medical service took army "rank," the chemist, whose services were of equal importance, not only took no

"rank" at all, but was made responsible to superiors having no special knowledge of his subject. This state of affairs, rendering as it did the public service of chemists an unattractive career to the best talent in the profession, was fraught with danger to the future well-being of the country, and was a short-sighted policy which, in time of trouble, might well lead to disaster. It was a matter which could not be lightly dismissed because it affected only a small number of chemists—it was a question of principle of far-reaching consequences, and it was to be hoped that the Royal Commission would give heed to the representations of the Institute.

Another move in this same direction was the re-arrangement of the Chemical Staff of the London County Council which had been carried out since the retirement of Dr. Clowes. Under the new scheme the Chemical Department—as an independent Department—ceased to exist, and the chemical staff was subordinated to the Medical Officer of Health. This, again, appeared to be a distinctly retrograde step, and one which the Institute could not but deplore. The matter had been represented to the Chairman of the County Council, Mr. Cyril Cobb, and he had made it perfectly clear that in this re-arrangement there had been no intentional slur cast upon the status of the chemical staff; but it was a dangerous precedent, and one which the Institute regarded with apprehension for several reasons. There was the impression left on the public mind that the services of the chemist were of less importance than formerly; whereas, in fact, as time went on they were certain to become more and more important. Further, there was conveyed the idea that the status of the professional chemist was an inferior one—in other words, that his profession was to be degraded in rank with corresponding exaltation of a kindred profession, a principle to which the Institute could not give its sanction.

The Council had also dealt with the conditions of appointments of Public Analysts, on which subject they had prepared a statement which had been published in the *Proceedings*, and would be issued to members of many local authorities. The Council hoped that, by this publication, the authorities might realise and appreciate more fully than they appeared to have done in the past the nature and responsibilities of these public officers.

In other branches of the profession, particularly in its applications to industry, the prospect for young chemists was improving. Not only was there little difficulty in placing Associates in appointments, but they were offered higher commencing salaries than formerly, and, although the cost of living had greatly increased, they were generally able to secure a "living wage" in most branches of the profession at the outset of their careers, which was much less frequently the case a few years ago.

Prof. Meldola then dealt at considerable length with the Report of the Conference of Professors of Chemistry, held under the auspices of the Institute in October last, which was attended by professors from practically all the principal educational centres of the country, the Institute thus providing an area for the free discussion of the broad question of the education of professional chemists. The Report of this important meeting was under the consideration of a Special Committee composed of representatives of every department of the profession—professors and teachers, private consultants, practitioners, and those who are accustomed to the scientific control of industries. Their task would be one of no little magnitude, and would probably effect considerable re casting of the Regulations of the Institute in the light of modern educational development. Whatever scheme might eventually be adopted it was certain that the Council would safeguard the status of the existing members. Professors and teachers would gladly welcome the support which the Institute might lend to their endeavours to raise the educational level to the required standard, while senates, councils, and governing bodies could not afford, on public grounds, to set aside curricula of studies, or to ignore a standard regarded as essential for efficient training for the chemical profession by a body fully representative of that profession. It was in this way that the influence of the Institute in the educational world might, through a revision of the existing Regulations, be exalted into a still greater power, making for the highest efficiency of the chemist of the future.

Sir William Ramsay, in proposing a vote of thanks to the President for his Address, endorsed the views which had been expressed with reference to placing men having no technical knowledge in the control of experts, and remarked on the absurdity of requiring them to sign reports only fully understood by the specialist. He also bore testimony to the fact that the Institute was of the greatest possible service not only to young professional chemists in securing them appointments, but also to manufacturers and authorities who required the services of such chemists. He hoped that the Conference of Professors of Chemistry would result in a working arrangement being devised to attract all properly trained and competent young chemists to the ranks of the Institute.

The vote was seconded by Mr. John Spiller, and carried unanimously.

The President, having replied, submitted the report of the Scrutineers.

The following were elected Censors:—Dr. George Beilby, F.R.S., Prof. Percy F. Frankland, F.R.S., Mr. David Howard, and Dr. George McGowan.

The Officers and Council for the ensuing year were elected as follows:—

President—Raphael Meldola, D.Sc., LL.D., F.R.S.

Vice-Presidents—George Thomas Beilby, LL.D., F.R.S.; Edward John Bevan; James Johnston Dobbie, LL.D., D.Sc., F.R.S.; Sir Alexander Pedler, C.I.E., F.R.S.; Sir Boverton Redwood, Bart., D.Sc.; Edward William Voelcker, A.R.S.M.

Hon. Treasurer—Alfred Gordon Salamon, A.R.S.M.

Members of Council—Leonard Archbutt; Robert Frederick Blake; Arthur George Bloxam; William Thomas Burgess; Cecil Howard Cribb, B.Sc.; Charles Frederick Cross, B.Sc.; Martin Onslow Forster, D.Sc., F.R.S.; Gilbert John Fowler, D.Sc.; Sir Richard Garton; Arthur Harden, D.Sc., Ph.D., F.R.S.; Otto Hehner; Charles Alexander Hill, B.Sc.; Edward Hinks, B.Sc.; William Richard Eaton Hodgkinson, Ph.D.; Alfred Henry Knight; Henry Rondel Le Sueur, D.Sc.; William Macnab; Gordon Wickham Monier-Williams, M.A., Ph.D.; Francis Richard O'Shaughnessy, A.R.C.S.; William Henry Perkin, LL.D., Ph.D., F.R.S.; Sylvester Oliffe Richmond; Clarence Arthur Seyler, B.Sc.; Thomas Stenhouse, jun., B.Sc., A.R.S.M.; Frederick Wallis Stoddart; Oliver Trigger; William Henry Willcox, M.D., B.Sc.; James Woodward, B.A., B.Sc.

Mr. W. J. A. Butterfield, Dr. Percy E. Spielmann, and Mr. Herbert F. Stephenson were elected Honorary Auditors.

With a vote of thanks to the retiring Officers and Members of Council the meeting terminated.

Institute of Chemistry.—Mr. William Macnab, F.I.C., will deliver the second lecture on "Explosives," on Thursday, March 26, 1914, at 8 p.m., at King's College, Strand, London, W.C., Prof. R. Meldola, D.Sc., F.R.S., President, in the Chair. *Syllabus.*—General description of Rules and Regulations prescribed by the Explosive Department of the Home Office for the construction and working of explosive factories. Description of processes and plant used in the manufacture of the principal explosives. "Permitted" explosives for use in fiery coal-mines, and the Home Office Test which they have to pass. Military propellants and the conditions which they have to fulfil. Recent filling material for shells. Sporting powders: general characteristics. Novel application of explosives. Scope of the chemist's work in connection with explosives.

NOTICES OF BOOKS.

Studies in Water Supply. By A. C. HOUSTON, D.Sc., M.B., C.M. London: Macmillan and Co., Ltd. 1913.

THIS monograph is practically a summary of papers and articles published by the author, embodying the results of his personal experiences and giving accounts of his investigations. Local authorities as well as those who are engaged in water analysis will find it very convenient to be able to procure a collection of all the author's valuable work carried out while he has been Director of Water Examination to the Metropolitan Water Board. While the book is essentially an account of the author's own experiences other publications are not altogether unnoticed, and they are always very impartially criticised. Many tables of results and graphical representations are given relating to bacteriological and chemical tests, and processes of purification and sterilisation are clearly described. The question of the connection between the purity of the water supply and the prevalence of disease is lucidly treated, and a valuable feature of the book is the detailed description of the routine methods of bacteriological work. Methods of collecting and labelling samples, registering results, and decimally diluting samples are first treated, and a chapter is devoted to the detailed description of the exact method followed in the examination of a sample of raw river water. Full accounts are included of each day's work, and the composition of the culture media used for the different tests is also given.

Les Catalyseurs Biochimiques dans la Vie et l'Industrie. ("Biochemical Catalysts in Life and in the Industries"). By JEAN EFFRONT. Paris: H. Dunod and E. Pinat. 1914.

THIS treatise on the proteolytic enzymes gives a detailed account of the work which has been done on the catalysts of nitrogenous matter. The preparation and properties of the individual enzymes, pepsin, trypsins, amidases, and the study of the products resulting from them are carefully described. Most of the numerical data given and the methods of analysis have been verified and tested by the author, who reveals in the text an extensive knowledge of his subject in all its branches. The book contains an important chapter on the coagulation of the blood, in which recent work is well summarised and critically examined. The applications of diastatic reactions in the industries are also treated, and the important parts played by the enzymes in therapeutics, brewing, tanning, &c., are admirably described, while the methods of analysis of the products of proteolysis which may be employed in the study of medical problems such as the process of digestion are also included.

Annuaire pour l'An 1914. Paris: Gauthier-Villars.

THE physical and chemical tables given in this annual published by the Bureau des Longitudes have been revised, and some interesting new articles have been added. These include one by M. Bigourdain on "Le jour et ses divisions," which gives a short account of the history of primitive methods of dividing the day, and also discusses the question of the unification of the astronomical and civil day and methods of transmitting the time. A second short article by M. Ph. Hatt deals with the deformation of images by telescopes.

Taschenbuch für die Anorganisch-Chemische Grossindustrie. ("Pocket-book for the Inorganic-chemical Major Industries"). By Prof. Dr. G. LUNGE and Dr. E. BERL. Fifth Edition. Berlin: Julius Springer. 1914.

THE fifth edition of this useful pocket-book is characterised by the same excellent features which deservedly won success for the earlier issues. The statistics and data have in all cases been accurately brought down to date, and many new tables of constants have been added, a great number being taken from Landolt's "Physikalisch-chemische Tabellen." New methods of analysis are also described, the experimental directions being very fully given, and every care has been taken to provide clear descriptions of reliable methods only. All numerical results have been recalculated on the values given by the International Atomic Weight Commission for the year 1913 on the basis O = 16.

CORRESPONDENCE.

ATOMIC WEIGHTS.

To the Editor of the Chemical News.

SIR,—If a Rydberg series (CHEMICAL NEWS, xcix., 149) be arranged for all the elements, consisting of odd and even whole numbers progressively differing by four units (= the atomic weight of a helium atom), it can be shown that the decimal fractions can be accounted for by considering the elements as mixtures of whole-number components selected therefrom, thus:—

Copper.	*Silver.*	*Gold.*
$63 \times 7 = 441$	$107 \times 7 = 749$	$196 \times 7 = 1372$
$67 \times 1 = 67$	$111 \times 2 = 222$	$200 \times 3 = 600$
8)508	9)971	10)1972
63·5	107·88	197·2

I believe that Prof. Soddy was the first to make an observation based upon radio-active experiments that the common elements might be mixtures, although Sir William Crookes in 1887 suggested that the atomic weights might be mean values.—I am, &c.,

F. H. LORING.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clviii., No. 4, January 26, 1914.

Chlorides of Iridium.—Marcel Delépine.—The author prepared a specimen of the yellow powder obtained by the action of sulphuric acid on the chloroiridites and then raised it to temperatures of 200°, 300°, 400°, 450°, and 500° in a current of dry hydrochloric acid gas for at least an hour. Progressive variations of composition then took place, and the composition gradually approximated to the formula $IrCl_3$. At 600° decomposition began with liberation of chlorine and formation of a mixture of reduced metal and anhydrous iridium chloride. Apparently the substances obtained, even at 500°, are not the anhydrous chloride but substances of formula $IrCl_3.mHCl.nH_2O$, where m and n are small fractions. The chlorides obtained up to 500° are distinguished from the anhydrous chlorides by their hygroscopicity and their solubility. The aqueous solutions of the chlorides prepared at 400°, 450°, and 500° can be concentrated. If the residue is redissolved and again evaporated a black mass is obtained which, after being dried at 100°, has very nearly the composition $IrCl_3.1·5H_2O$.

Vol. clviii., No. 5, February 2, 1914.

Alkylation of the Cyclopentanones and Rupture of the Cyclic Chain of Tetraalkyl Derivatives by Sodamide.—A. Haller and R. Cornubert.—α-Methylcyclopentanone can be prepared by methylating ethylcyclopentanone carbonate and decomposing the substituted ether by means of concentrated hydrochloric acid. The di-, tri-, and tetra-compounds can be prepared by successive methylations. The boiling-points of these derivatives increase regularly with the number of methyl radicles, while the reverse is the case for the densities and indices of refraction. α-Methylcyclopentanone fixes only two allyl groups. When sodamide acts on tetramethylcyclopentanone the amide of 2.2.5-trimethylcaproic acid is obtained.

Influence of Shaking upon the Solution of Copper in Nitric Acid.—Maurice Drapier.—When copper is dissolved in nitric acid solution no longer occurs, or else progresses slowly, when the liquid is shaken. It might be supposed that this is due to the fact that the heat of solution produces a local elevation of temperature which shaking renders impossible. Experiments, however, show that this explanation is not correct. If a stick of copper is made to rotate on its axis at different rates in solutions of nitric acid it is found that the quantity of copper dissolved in a given time first slowly diminishes as the rate of rotation increases. Above this critical rate the velocity of solution rapidly decreases and finally vanishes. The critical rate increases with the concentration of the acid. It is possible that the solution of copper in nitric acid is an autocatalytic reaction, and the agitation of the solution by diluting the products of reduction of the acid puts off the moment at which their concentration reaches the stage at which the reaction is appreciably catalysed.

Bulletin de la Société Chimique de France.
Vol. xv.-xvi., No. 2, 1914.

Reaction of Succinic and Malic Acids.—W. Œchsner de Coninck.—A concentrated aqueous solution of succinic acid is added to some grms. of calcium salicylate in a little cold water, and the whole is gently heated. A pale pink coloration soon appears. This coloration is very stable, and in the author's experiments it persisted for eight days, even when the flask was exposed to sunlight for some hours each day. With malic acid a similar coloration is obtained, but it is not so stable, and if the liquid is gently boiled for fifteen to twenty minutes the colour fades. After some hours the liquid becomes a light yellowish brown. This reaction can be employed to verify the presence of succinic or malic acids in a liquid.

MISCELLANEOUS.

Royal Institution.—On Tuesday, March 24, at 3 o'clock, Mr. A. H. Smith, Keeper of Greek and Roman Antiquities in the British Museum, begins a Course of two lectures at the Royal Institution on "Landscape and Natural Objects in Classical Art"; and on Thursday, March 26, Dr. C. W. Saleeby delivers the first of two lectures on "The Progress of Eugenics—(1) The First Decade 1904—1914; (2) Eugenics of To-day, its Counterfeits, Powers, and Problems." The Friday Evening Discourse on March 27 will be delivered by Prof. J. A. Fleming on "Improvements in Long Distance Telephony"; and on April 3, by Prof. Sir J. J. Thomson on "Further Researches on Positive Rays."

Faraday Society.—A General Discussion on "Optical Rotatory Power" will take place on Friday, March 27 next, in the rooms of the Chemical Society, Burlington House, London, W. The meeting will be open to Fellows of the Chemical Society and Members of the Physical Society of London. Others interested in the subject and desirous of being present should apply to the Secretary of the Faraday Society. The following provisional programme has been arranged:—

5.0. Prof. H. E. Armstrong, F.R.S., will preside at the Afternoon Session and deliver an Introductory Address. Prof. Dr. Hans Rupe (Basle) will read a paper on "Some Contributions to the Knowledge of the Influence of certain Groups on Rotatory Power." Prof. Dr. H. Grossmann (Berlin) will read a paper on "New Studies in the Rotatory Dispersion of Tartaric Acid and Malic Acid." Dr. E. Darmois (Paris) will read a paper on "The Existence of Racemic Tartaric Acid in Solution." Prof. Dr. Leo Tschugaeff (St. Petersburg) will communicate a paper on "Anomalous Rotatory Dispersion." Dr. T. M. Lowry and Mr. T. W. Dickson will read a paper on "Normal and Anomalous Rotatory Dispersion."

6.30—8. The meeting will adjourn for Dinner at the Trocadero Restaurant.

8.15—10. Prof. Percy F. Frankland will preside at the Evening Session. Dr. T. M. Lowry and Mr. H. H. Abram will exhibit some apparatus for measuring Rotatory Dispersion, and will read a paper on "An Enclosed Cadmium Arc for Use with Polarimeter." Dr. R. H. Pickard and Mr. J. Kenyon will read a paper on "The Relations between the Rotatory Powers of the Members of Homologous Series." Dr. T. S. Patterson will read a paper on "The General Behaviour of Optically Active Compounds as regards the Dependence of Rotation on Temperature, Dilution, Nature of Solvent, and Wave-length of Light." The meeting will then be open for general discussion.

MEETINGS FOR THE WEEK.

MONDAY, 23rd.—Royal Society of Arts, 8. (Howard Lecture). "Surface Combustion," by Prof. W. A. Bone, F.R.S.

TUESDAY, 24th.—Royal Institution, 3. "Landscape and Natural Objects in Classical Art," by A. H. Smith, M.A.

WEDNESDAY, 25th.—Royal Society of Arts, 4.30. "Fashion in Art," by Sir Charles Waldstein, Ph.D.

THURSDAY, 26th.—Royal Institution, 3. "The Progress of Modern Eugenics," by C. W. Saleeby, M.D., &c.

— Royal Society. "Nature of the Tubes in Marsupial Enamel and its bearing upon Enamel Development," by J. H. Mummery. "Oxidation of Thiosulphate by certain Bacteria in Pure Culture," by W. T. Lockett. "Production of Anthocyanins and Anthocyanidins," by A. E. Everest. "Variations in the Growth of Adult Mammalian Tissue in Autogenous and Homogeneous Plasma," by A. J. Walton. "Decomposition of Formates by *B. coli communis*" and "Enzymes which are concerned in the Decomposition of Glucose and Mannitol by *B. coli communis*," by E. C. Grey. "Description of a Strain of *Trypanosoma Brucei* from Zululand—Part I., Morphology; Part II., Susceptibility of Animals," by Surg.-Gen. Sir D. Bruce, Major A. E. Hamerton, Capt. D. P. Watson, and Lady Bruce.

— Chemical, 4.30. (Annual General Meeting). President's Address, "Recent Researches on Tautomerism."

FRIDAY, 27th.—Royal Institution, 9. "Improvements in Long Distance Telephony," by Prof. J. A. Fleming, F.R.S.

— Faraday Society, 5. General Discussion on "Optical Rotatory Power."

— Physical, 5. "New Type of Thermogalvanometer," by F. W. Jordan. "Instrument for Recording Pressure Variations due to Explosions in Tubes," by J. D. Morgan. "Direct Measurement of the Napierian Base," by R. Appleyard. "Experiment with an Incandescent Lamp," by C. W. S. Crawley.

SATURDAY, 28th.—Royal Institution, 3. "Recent Discoveries in Physical Science," by Prof. Sir J. J. Thomson, O.M., F.R.S.

ERRATA.—P. 117, col. 2. At bottom *read*:—"It is true that $\frac{dP}{dx}$, $\frac{dp}{dx}$, and $\frac{dp_2}{dx}$ are all zero. It is, however, not necessary that $\frac{dP}{dy}$ shall also be zero, and hence $y = x$. $\frac{dP}{dy}$ does not change signs," &c. At top of p. 118, the vinculus should only include $\overline{y-x}$, and not $\overline{y-x\mathrm{P}}$.

THE CHEMICAL NEWS.

Vol. CIX., No. 2835.

NOTES ON PLANT CHEMISTRY.

By P. Q. KEEGAN, LL.D.

Incidents of Analysis.

The utility of what is known as Millon's reagent in plant analysis is occasionally very evident. The proper way to prepare it for this purpose is as follows:—Place some red HgO at the bottom of a long narrow test-tube, add a few drops of water to moisten, and then some glacial acetic acid, warm, not boil, till the oxide is dissolved, and then immediately pour the solution into a bottle, which stopper well and keep in the dark. After a time crystals form in the liquid, but never mind; when using it shake well up, and pour at once two or three drops into the solution to be tested, add one or two drops dilute solution of KNO_2, and slowly warm, when the coloration will appear. In this way we obtain in most cases a coloured solution and not a precipitate, which latter frequently occurs when the reagent is prepared by dissolving precipitated HgO in dilute acetic acid.

Occasionally it is very difficult to obtain well formed crystals of oxalate of calcium from leaves under analysis in the ordinary course, *i.e.*, by the last extraction by dilute HCl. In this case wash the final residue on the filter with water, and dry it or leave it to dry in the air, then powder a portion of it very fine, pour over it placed in a bottle strong HCl, diluted with equal volume of water, and cooled; leave for five days, filter off the solution, and add sufficient solid acetate of soda and a little acetic acid to precipitate the oxalate; stand one day, decant, wash the crystals, and examine under the microscope, when an extraordinary success will be reported. Two particularly bad cases, viz., the leaves of beech and of water-lily, yielded by this treatment magnificently clean and beautifully formed crystals of oxalate, wherein the crossed markings and colour contrasts were clearly visible by the light of an ordinary condenser.

A recent statement by Lloyd, that "in certain cells of the pericarp of fruits the tannin exists in a sort of solid solution with a pectose which absorbs it, and hence it cannot be extracted," is hardly referable to fruits only. According to my own experience it is very difficult and sometimes impossible to extract all the tannic matter from either leaves or barks. In the case of very mucilaginous leaves or roots alcohol frequently extracts no tannin at all, *e.g.*, species of buttercup, comfrey root, &c., and it requires two or three relays of boiling water and concentration of the solutions before a sufficient amount is extracted, even for purposes of mere qualitative recognition. In some cases the second aqueous extract contains probably twice as much tannin as the first, and it must needs be that these facts were unknown to some of the old analysts, otherwise their reports would in many important instances have been fuller than they are. Owing to the difficulties of the extraction of tannin from the material and of its complete purification from tannoid, &c., any attempt to determine its quantity accurately is in most cases hopeless. Then, again, there is the question of the instability, impurity, &c., of gallotannin especially. The decomposition of a catechol tannin might take place in two ways, viz., by a kind of absorption of it by a pectose followed by the production of a brown "humin" quite refractory to fused alkalis, or also of a partial transformation of its phenolic groups, or rather of an addition to their number. This is evidently the case with the bark and leaves of oak, beech, and Spanish chestnut. All these tannins give the HCl vanillin reaction decisively, but do not give the iodine test for gallotannin quite satisfactorily; with Millon's reagent they sometimes turn blue, but at other times there is a green precipitate only, or a deep red and green dichroic solution. The tannin of certain Rosaceæ and of Saxifragaceæ behave in a very similar way, but in my opinion there is nothing very serious in these facts; *i.e.*, there is no great magical alchemy in the partial transformation of a catechol tannin into gallotannin, while the phloroglucol group thereof remains intact. In fact, there are cases, *e.g.*, that of *Ribes sanguinea*, known as the flowering currant, where the whole of the catechol group has apparently been destroyed, leaving nothing but a voluminous red phlobaphene and a quantity of phloroglucol; so that you have the rather startling phenomenon of an apparently catechol tannin yielding no protocatechuic acid on fusion with potass. A study of the vigorous physiological processes, in many cases assuming the character of pathological ones, going on in the barks of trees and shrubs, indicates that intense chemical changes take place also in connection therewith. The normal progress of the thickening growth of the axis of the tree reacts powerfully on the tissues of the cortex, inducing sclerosis or destruction of its external tissues, hypertrophy, flattening of the cells, formation of periderm and rhytidome, &c. In all these cases there is an intense absorption of oxygen, *i.e.*, there is a co-operation of the chemical energies immanent in the system which is constituted by the plant itself in conjunction with the oxygen of the air. The oxidation varies considerably in intensity according to the anatomy or histology or pliancy of the various organs, and this fact would account for the varying amount of gallotannin, or perhaps gallic acid found in bark, wood, or fruits of certain species of oak, beech, Spanish chestnut, and other Cupuliferæ.

In the course of studies on anthocyan it was found necessary to trace the connection between certain specially vivid or beautiful colours shown by certain flowers and the decomposition products of the tannins which the plants bearing these flowers produce. In other words, it was sought to prove what some enquirers had denied, viz., that a chromogen of anthocyan does actually exist. And as gardeners had apparently cultivated a blue variety of the Chinese primrose, a few species of the order Primulaceæ were examined. Both the young and old leaves of the common primrose were found to contain tannoid only, though there seemed to be a little tannin in the leaves got in June on the outskirts of a wood in a damp rocky locality; the flower stock and flowers, however, contained considerably more tannin which was phlobaphenic, gave the vanillin HCl reaction decisively, and precipitated gelatin, the precipitate being tinged deep blue by solution of iron alum. The leaves of the yellow loosestrife were found to contain tannoid and a tannin reacting precisely as that of the primrose, and all the more distinctly inasmuch as its quantity was much greater. Another plant, the sea pink, belonging to an allied order, was analysed; it contained what may be called a tannide, yielding reactions similar to the above, except that with vanadate of ammonium a blue colour, with peracetate of iron a blue-violet precipitate, and with nitrate of silver a beautiful red coloration were produced; on potass-fusion it yielded phloroglucol only, whereas in the other two cases protocatechuic acid was also obtained. All three were phlobaphenic, and all on careful warming with dilute HCl yielded an extremely beautiful red solution vividly recalling as to tint and otherwise the pigment which decorates the petals of the well-known winter primula of the greenhouse. On the strength of this investigation it was concluded that there is a clear genetic connection between tannin and pigment and that the natural species (carniola, frondosa, sapphirina) or the cultivated varieties or hybrids (sinensis, &c.), of

primula are not true blues, but rather what a horticultural writer describes as a "wishy-washy lilac-cum-lavender-cum-purple" affair.

It is not surprising that the HCl-vanillin reaction for phloroglucol should have attained great prominence. As a macro reagent on the tissues it is worthless. The correct coloration that should ensue on its application is a rather dull vermilion-red, and not a violet or purple-red. Waage's famous histological researches (1890) over the presence of phloroglucol in plants are surprisingly accurate in the main, but it is doubtful if there exists, as he states, any phloroglucol tannin in cornus, crocus, œnothera, coffee, peucedanum, scorzonera, clematis, strophantus, lilac, viburnum, symphoricarpus (all except the first three contain caffetannin or caffeic acid). He finds no phloroglucol in the examined Rutaceæ, Caryophyllaceæ, Cruciferæ, or Papaveraceæ; but he rather overlooks the Primulaceæ and Plumbagineæ, which contain several species producing splendid tannins or tannides that yield the HCl-vanillin reaction decisively. It is necessary to evaporate to dryness a little of the purified alcoholic or aqueous extract of the leaves, &c., add a little vanillin and a drop or two of HCl, when the dull vermilion-red will immediately appear. Extracts of plants which contain pure gallotannin, caffetannin, or tannoid only do not yield the reaction, and it is most advisable to purify by alcohol all aqueous solutions or extracts containing gallotannin or gallic acid before applying the test, otherwise a dirty violet colour, due apparently to "humin" or to a high anhydride, sometimes appears, which may prove seriously misleading.

The paper by Prof. A. G. Perkin on "Quercetagenin," published in *Trans. Chem. Soc.* (1913), is, from a purely scientific point of view, of the utmost value and importance. Therein for the first time, so far as I know, it is recognised by a professed investigator that a certain flavonol derivative (tannoid) contains a nucleus with a quinol grouping in place of the ordinary phloroglucol nucleus. I might here, however, take the liberty of stating that on four different occasions in my published papers I asserted the existence of a quinol nucleus in the tannoids of certain plants belonging to the Compositæ and Labiatæ orders. I considered that there must be present somewhere a tannoid corresponding to caffetannin, and it would seem now to be settled that what bears the name quercetagenin represents that required substance. What is remarkable is that it has apparently never before been sought for and distinguished specifically by those whose means and instruments of research are superior to mine.

Some years ago the botanical world was startled when some enterprising Scot had discovered a blue poppy on the Himalayan mountains. Since that period several other blue poppies have been discovered, and a large area of western China and thereabouts has been christened "the land of the blue poppy." All these are of the genus *Meconopsis*, and, in fact, *M. speciosa*, of a glorious Cambridge blue, is reckoned one of the most beautiful flowers in existence. Fortunately there is one native species, the Welsh poppy (*M. cambrica*) of this genus in England, and as it is found in this valley, I secured a few leaves thereof, and analysed them with special reference to the existence therein of a chromogen precursive of a true blue pigment. The leaves were very mucilaginous, and hence on boiling them with alcohol no tannic matter was extracted; the residue, however, was dried and boiled twice with water, and both extracts, on purification from mucilage, &c., gave decisive reactions of caffetannin. Thus it would appear that this blue poppy sensation was no sham, and in accordance with the results of my previous researches the petals of this genus of plants were adjudged competent to evolve a pure blue pigment. The leaves contained much nitrate, and also much oxalate of calcium in large fine crystals. Their ash yielded 43·6 per cent soluble salts, 3·3 silica, 26·3 CaO, 4·2 P_2O_5, 6·6 Cl, 12 SO_3, and only a little iron and manganese.

Patterdale, Westmorland.

NATIONALISATION OF SOURCES OF RADIUM IN UNITED STATES.*

Report of Committee on Mines and Mining.

(Concluded from p. 138).

Foreign Demand.

As already stated, by far the larger part of the radium ore so far produced in the United States has been shipped abroad, and, even worse than this, that portion of the radium which is being extracted in America has also been largely contracted for foreign delivery. This has opened up to foreign medicine and science opportunities for the investigation and treatment of malignant diseases that have been denied to the American people, except by purchase of manufactured radium compounds at almost prohibitive prices. To-day there is probably less than 2 grms. of radium salts in the possession of physicians in America, which, considering the almost miraculous cures of cancer shown to the Committee by reputable surgeons through the means of plaster casts and photographs, is appalling. In Europe a very different condition exists. During the past year extensive appropriations have been made there for the purchase of radium and mesothorium, showing the great demand that has arisen for these materials in the treatment of cancer. Some of these purchases have been made by Government appropriation and some by municipal or other public subscription. The Austrian Government has expended 600,000 dols. for the purchase of deposits of radium-bearing ores, and has made subsequent provision for the mining of these ores and the extraction of the radium. Prussia has appropriated 370,000 marks for the purchase of 1 grm. of radium bromide.

Radium in Cancer Work.

Three leading surgeons of America who have themselves had extensive experience in the application of radium in the treatment of malignant diseases, viz., Dr. Howard A. Kelly, of Baltimore; Dr. Robert Abbe, of New York; and Dr. Curtis F. Burnam, of Baltimore, have appeared before the Committee, and have shown casts and photographs of cancer cures actually brought about in their practice, which appear to the Committee to be in themselves more than sufficient argument for the proposed legislation. These three surgeons and Dr. H. R. Gaylord, Director of the New York State Cancer Laboratory, have favoured the general principles outlined in this Bill, have expressed their inability to procure more radium for their own practice, and have emphasised their great need and desire for more of this material to be used in treating the sufferers of the most malignant of diseases. Large sums are appropriated each year for the treatment of the diseases of animals, for the destruction of pests, and various sums for other important objects for the benefit of the people. It has been demonstrated beyond a doubt that this remedy is a cure for external malignant growths.

Hoffmann, the statistician, estimates that each year 75,000 people die from these growths known as malignant. If this remedy will cure 20 per cent we have saved 15,000 lives each year. The cause of cancer is to-day unknown, so physicians must apply themselves to the cure until someone discovers the cause, so that it will be known how to prevent this disease.

If the Government does not secure these ores bearing radium it is quite likely that large quantities will be shipped out of the country, and what is extracted in America will fall into the hands of those who will have a monopoly, and the price will be so high that it will be out of the reach of poor people. As it has been well said, "cancer is the poor man's disease, and radium is the rich man's remedy."

* Slightly abridged from *Report* No. 214 of the House of Representatives, 63rd Congress, 2nd Session.

If this Bill becomes a law it may be hoped that in time the Government will control this remedy so that it may be placed in all parts of the country, readily accessible to all those who may be so unfortunate as to require its use, and may secure the treatment without having to pay an exorbitant price. It is certainly better for the Government to have the monopoly than the private individual in so important a curative agent for disease, with which no one can be assured they will never be afflicted.

It is now estimated that the hospitals belonging to the United States ought to have at least 25 grms., and at the present price it would cost 120,000 dols. per grm., which would mean the expenditure of a large sum to secure the amount thought necessary. It has been shown that foreign buyers have been securing all the ore they could and shipping it to their own country and extracting the metal, and then the Americans have been obliged to buy the radium from them. It is important that the American people should have the control of the remedy which lies in the public lands which the Government now owns.

Radium Institutes.

Several radium institutes have been founded throughout the world for studying the application of radium to science and to disease. Some of these are private and some are public. Prominent among them may be mentioned the Radium Institute of Austria, founded under a donation given by Dr. Kuppelweiser to the Academy of Science of Austria, which now has one of the largest supplies of pure radium salts used chiefly in scientific investigations. In Paris a new radium institute under the direction of the Sorbonne has been built by this University near the Pantheon. In England the London Radium Institute was founded by Sir Ernest Cassel and Viscount Iveagh, who gave a large sum for its endowment. This Institute is making a special study of the application of radium to disease. In America the National Radium Institute has recently been founded by Dr. Howard A. Kelly, of Baltimore, and Dr. James Douglas, of New York.

Difficulty of Securing Radium on any other Basis than Government Operation.

At present, on account of the tremendous demand for the material abroad, there is no means of keeping radium ores or radium in America, except by overbidding the excessive price now being offered for them in European markets; and this means that the American people must buy back from foreign countries at speculative and exorbitant prices the very radium which was their own, and which their Government has allowed to become subject to foreign exploitation. It has already been shown that foreign Governments and municipalities are prepared to pay prices for radium far in excess of the cost of production and manufacture, and they have already obtained more than half of the available ores produced in the United States. It was in France, Germany, and Austria that the value of radium was first appreciated. Here a demand for it was first established and processes for extracting it from these ores were developed. Meanwhile the American Government has been giving away its deposits of radium-bearing ores, which even though limited are the most extensive known, and allowing them to pass into the ownership of a foreign corporation, a few American companies acting as shipping agents for other foreign corporations or to an American company which sells its radium largely to foreign purchasers. The high price of radium salts —by far the larger part of this price representing a profit to the manufacturer—is taking radium out of the country, and even if it stays in the country the present price makes its use so expensive that the material can hardly be expected to be available to people of small means, except in so-called charity cases. Accordingly it seems extremely important that the United States Government shall make such provision as shall be necessary to obtain supplies of radium requisite to meet the more urgent needs of the American people. The responsibility for this neglect and delay in development in the United States rests with the scientific men in the universities, with the Government service, and with Congress itself. The legislation now proposed is intended to remedy this situation.

Appropriations.

The Committee after due deliberation has asked for an appropriation of 150,000 dols. for the erection and general equipment of a suitable building or buildings for radium extraction and other work of the Bureau of Mines in the metal-mining States, and the further sum of 300,000 dols. for the necessary expenses connected with the purchase and treatment of radium-bearing ores and the extraction of radium therefrom during the fiscal year ending June 30, 1915. The Committee believes that these amounts are less than should be allotted to this important work, but believes also that they will be sufficient for the erection and equipment of the extraction plant and the purchase of such ores as can be procured in the fiscal year 1915, and will enable the department to get the work well under way. It is expected that the buildings to be erected under this appropriation of 150,000 dols. will be inexpensive structures that will be located at points best adapted to the success of this radium work. The larger part of this appropriation is for the engineering equipment necessary in the concentration and treatment of the ores and the extraction of the radium. The other appropriation (300,000 dols.) will be used for the purchase of ores (covering the cost of mining) and for the chemical equipment and supplies and general operating expenses. It is expected further that if the necessary supply of ore be obtained the commercial value of the radium extracted under this appropriation will be far in excess of the total amount of the appropriation authorised in this Bill.

The Committee believes that the welfare of the American people and especially the alleviation of those suffering from that terrible malignant disease, cancer, demand that this Bill be passed, and that this important work be initiated without undue delay.

THE SCIENTIFIC WEEK.

(From Our Own Paris Correspondent).

A Radium Paratonnerre.

Whereas the pointed lightning-rod has no preventive action, and only a limited local action, M. Szilard has discovered that by supplying it with a screen furnished with radium (1 to 2 milligrms. suffice), it is possible to give it most interesting qualities. The radium renders the layers of air (even those far removed from the point) several millions of times more conductive than is ordinary, and this effect produces an exchange of electricity between the different superposed atmospheric layers. Simultaneously an outlet of electricity is produced between the atmosphere and the Earth, and that happens, not only in a fashion limited to the point, but by a constant uninterrupted current passing through a layer of air with a radius of several dozens of metres, which the progressive conductibility of the air towards the point concentrates towards its direction. And this conductibility is so much the greater in proportion to the strength of the electrisation of the atmosphere. But if, in spite of all preventive action great discharges are produced, they undergo at the same time the effect of the conductibility of the air which will transport them from a pretty considerable distance to the paratonnerre, and the priming effect that the radio-active rays exercise on the sparks in making them flash out in a primitive state of development. We have thus a lightning-rod that is preventive against all the electric manifestations of the atmosphere and a paratonnerre with

a large radius of action. The paratonnerre of this principle realised by M. Szilard has enabled him to verify and even measure these actions. The results have proved superior, from all points of view, to those obtained by ordinary paratonnerres. It is curious to remark that a Geissler tube oined to the new paratonnerre is lighted even in calm weather. These encouraging experiments merit to be continued in a large measure.

New Cultures of an Edible Mushroom.

For the last twelve years Prof. Louis Matruchot has been making lengthy experiments with a view of seeking out the influence of the conditions of environment on a new cultivable species of edible mushrooms, called the "blue foot," or *Tricholoma nudum*. The experimentation on these fleshy mushrooms is the more difficult seeing that their evolution is exceedingly slow. The cultures of blue-feet have been established on ricks or heaps of beech leaves in the cellars of the Paris Observatory; that is to say, in complete obscurity and in a temperature of 11°. The species cultivated by the method of M. Matruchot becomes modified. It produces in all seasons instead of only in the autumn. In a state of nature the blue-foot, an autumnal species, is rarely to be seen excepting in the period from October to December. In his trials of culture in collaboration with M. Costantin, of the Natural History Museum, M. Matruchot has gathered mushrooms at periods from January to July. With the new cultures, in the cellars of the Observatory, there has not been a single month in the year when he has not been able to gather the blue-feet. The proof is then made, that this edible and much sought after species can fructify, if it is cultivated, in a deep cellar at all seasons of the year. The culture in cellars with the help of indefinitely grafted mycelium makes great modifications appear in the general form of the mushroom, and this to such an extent that certain characteristics of the blue-foot species have become progressively attenuated until at last they have entirely disappeared. The individuals have taken a very marked gigantic character; the hat of 4 cm. in diameter, the stalk from 15 to 18 cm. high, excessively thick and humified. Also the violet tint so characteristic of this mushroom, from which it has taken its popular name of "blue foot," no longer exists neither on the stem which is white nor on the blades which are of a creamy colour, nor on the hat which is of a silky white hardly tinted with a very light shade of coffee and milk, which shade has progressively replaced the original nut-brown colour. The modifications of form and colour have not appeared all at once excepting as far as concerns the enormity of the stalk. M. Matruchot concludes that these experiments teach us that the *Tricholoma nudum*, cultivated in cellars, in the dark, at 11°, in a normally hygrometric atmosphere, vegetates as vigorously as in a state of nature. The blue-foot being able to produce in all seasons gives a continuous harvest. Moreover, every winter the white mushroom can be grafted with the help of young filaments taken from a culture of the preceding year. Thus it is possible to perpetually renew the culture, which is not the case with the mushroom of ordinary beds that are cultivated in quarries. Lastly, the delicate taste and aniseed perfume of the blue-foot subsists integrally, which indicates that the profound chemical qualities of the cellules is not sensibly modified. It is this same species that MM. Costantin and Matruchot in previous researches had cultivated in the open air, but without obtaining a sufficient return.

Aeroplanes and Marine Birds.

For a year past Dr. Magnan, Director of the Ecole des Hautes Etudes, has been collecting very numerous documents concerning the flight of birds. In a most rigorous manner he has calculated the alar surface, the weight of the wings, the spread and breadth of the wing, the total length of several hundreds of birds, at the same time as he studied the method of flight employed by the bird that he was studying. He has remarked that the different relative dimensions were, as it were, constant for the same diurnal birds practising the same kind of flight. Thus all diurnal birds of prey have very sensibly the same alary surface; the relation of their wing spread to the length of their body is, so to say, constant. On the other hand, these dimensions differ considerably when one examines different groups of birds, as rapacious birds, palmipeds, marine birds, sparrows, &c. In seeking for the characteristics of marine palmipeds he has been able to define these characteristics thus:—Marine palmipeds possess the largest relative wing spread of all birds; on the other hand, they possess, so to say, the narrowest wing. Their alar surface is very great, though less than that of the rapacious birds. Their tail is considerably shortened. Their total length is about the same as that of birds of prey in spite of the shortness of the tail. Lastly, the relation between the spread and the width of the wing is the greatest. M. Magnan shows, moreover, that the narrowness of the wing and the shortening of the tail seem to be the consequence of an adaption to the flight in the great currents of air, since all aquatic birds (ducks, little waders) that fly in like conditions, have also a narrow wing and a short tail. M. Magnan had already proved by his study on hovering birds that it was possible to apply to aeroplanes the dimensions found by him in birds, and to make practical applications of the same. It is thus that the Pomier monoplane piloted by Vedrines in the race for the Gordon-Bennett cup in 1913 was the first application, and, at the same time, the justification of these researches. The *fusslage* (yards, &c.) of this monoplane present absolutely personal characteristics; according to the indications resulting from the work of M. Magnan it has the weakest relation of the total length to the spread. This reduction of the fuselage has permitted very rapid risings from the ground, and seems to give a superior ascensional force, since the avion of the Biclovucie cavalry type has attained the height of 1500 metres in five minutes. M. Magnan has calculated (as for the hovering apparatus copying the rapacious birds) the dimensions of a monoplane that would copy marine birds. He has found for an apparatus weighing 400 kilogs. in marching order:—

	Hovering monoplane, rapacious type.	Monoplane, type of marine birds.
Alary surface	12·60 metres	10·20 metres
Weight of wings ..	78·800 kilogrms.	77·800 kilogrms.
Spread..	9·78 metres	10·30 metres
Width of wings.. ..	1·69 metres	1·25 metres
Length of tail	1·90 metres	1·32 metres
Length of the apparatus	4·34 metres	4·26 metres

As will be seen, there are very notable differences between these two types. It might perhaps be advisable for builders to take these data into consideration in totality or partially for the construction of hydroplanes.

Cooling of the Earth.

A French mathematician, M. A. Veronnet, has just made a series of ingenious calculations, the aim of which was to determine the evolution and the duration of the earth. This is a question that for a long time past has been haunting the minds of seekers. Is the earth to finish her existence by meeting, in her vagabond course, some wandering planet? Is a formidable shock to scatter into space the earthly continents in an infinite number of fragments? This is one of the numerous hypotheses that have been considered by scientific men. Other theories have, however, been brought forward. For certain students the disappearance of the carbonic acid of the air would cause the cooling of the earth, and the consequent disappearance of all animal and vegetable life. For others, again, it is the water that would disappear from the surface of the globe, and our globe is thus destined to die from drought. But the most general opinion is that the earth will die of cold when the sun can no longer send us the beneficent

heat brought to us by its rays. Since the earth solidified the flux of internal heat is very weak, and its temperature at the surface depends almost entirely on the heat received from the sun. Now, in past times, when a ray of sun attained one and a-half the power of the present rays of sun—which must have been the case about two millions of years ago—the temperature must have reached 90° at the latitude of 80°. The appearance of life cannot go beyond that period, and according to M. Veronnet it must have begun in the proximity of the poles. M. Veronnet has also calculated that in a little less than two millions of years a ray of sun being reduced by about only one-tenth, the temperature will have fallen on the earth to below zero even at the Equator. The surface of the earth will be completely frozen, and life on it will be almost impossible. According to this same scholar the planet Mars has been thus frozen for a long time past. Thus the dreams of astronomers and poets who affirm that Mars is inhabited are disappointed. Mars is a block of ice, according to mathematicians, and the earth has only two millions of years to live. Alas, this conclusion is not very consoling.

COAL IN THE WORLD IN 1913.

The production of coal in the whole world, according to the last official statistics, may be estimated for 1913 at 1250 millions of tons, compared with 1245 millions of tons in 1912, 1184 millions of tons in 1911, and 500 millions of tons in 1910. The greater part belongs to the United States, with about 40 per cent of the total production, Germany and England come next with 21 per cent each; then, in order of importance, France, Russia, Belgium, Austria, Hungary, and Holland. The European production for 1913 may be estimated at 550 millions of tons, the consumption of which may be reckoned in the following manner:—Consumption of the mines, 38 millions of tons, or about 7 per cent; metallurgy, 192,500,000 tons, or about 35 per cent; railways, 55 millions of tons, or about 10 per cent; stocks for navigation, 55 millions of tons, or about 10 per cent; gas and electric lighting, 44 millions of tons, or 8 per cent; industry, 82,500,000 tons, or 15 per cent; domestic consumption, 82,500,000, or about 15 per cent. As is seen by this it is metallurgy, industry, and domestic consumption that require the largest quantities of coal.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, March 12, 1914.

Sir WILLIAM CROOKES, O.M., President, in the Chair.

PAPERS were read as follows:—

"*Note on a Functional Equation Employed by Sir George Stokes.*" By Sir JAMES STIRLING, F.R.S.

1. In a paper by Sir George Stokes "On the Intensity of the Light Reflected From or Transmitted Through a Pile of Plates" (published in the *Proceedings* for 1862, see his "Math. and Phys. Papers," iv., 148-9), the author orms and solves two functional equations, viz.:—

$$\phi(m+n) = \phi(m) + \phi(n)\{\psi(m)\}^2/\{1-\phi(m)\phi(n)\},$$

$$\psi(m+n) = \psi(m)\psi(n)/\{1-\phi(m)\phi(n)\},$$

these equations being treated as independent.

2. The main object of the paper of Sir George Stokes is physical, not mathematical; and the purpose of the present note is to call attention to mathematical points not explicitly dealt with by him, viz.:—

(*a*) The two functional equations are not independent, the second being capable of being deduced from the first.

(*b*) The results arrived at by Sir George Stokes may be derived from the first equation alone and constitute the general solution of that equation. No such general solution of the second equation has been obtained.

"*The Mercury Green Line $\lambda = 5461$ as Resolved by Glass and Quartz Lummer Plates and on its Zeeman Components.*" By Prof. J. C. MCLENNAN and A. R. MCLEOD.

"*Electrical Condition of a Gold Surface during the Absorption of Gases and their Catalytic Combustion.*" By HAROLD HARTLEY.

At the suggestion of Prof. W. A. Bone, the author has carried out experiments on the electrical conditions of a gold surface during its absorption of hydrogen, carbon monoxide, and oxygen respectively, at temperatures between 300° and 400°, in order to establish certain data relative to surface combustion phenomena.

The results have proved (1) that the metal acquires a *negative* charge during the catalytic combustion of gases in contact with it (thus confirming previous unpublished observations by Bone and Makower), which effect is probably antecedent to the actual combustion, and primarily due to "occlusion" phenomena; (2) that the metal becomes *negatively* charged (0·5 to 1·5 volt) during the occlusion of the combustible gas (hydrogen or carbon monoxide), and *positively* charged (0·8 volt) during the occlusion of oxygen; and (3) that such electrical effects are probably due to occluded gas which is *leaving* (rather than *entering*) the surface. Any cause, such as a sudden lowering of the temperature, which would momentarily check the outflow of occluded gas, diminishes the intensity of the charge, whilst, conversely, a sudden diminution in the external gaseous pressure in the vicinity of the metal, temporarily increases it.

The experiments indirectly lend suppor to the view that the well-known electronic emission from incandescent solids is probably dependent upon the occlusion of gas.

"*Diffusion of Electrons Through a Slit.*" By J. H. MACKIE.

The paper deals with a comparison of the solutions of the two equations—

$$\frac{\partial^2 n}{\partial x^2} = 2\lambda \frac{\partial n}{\partial x}$$

$$\frac{\partial^2 n}{\partial x^2} + \frac{\partial^2 n}{\partial y^2} = 2\lambda \frac{\partial n}{\partial x};$$

the value of n being subject to certain prescribed boundary conditions. The equations arise in connection with certain experiments by Prof. Townsend and Mr. Tizard on the Diffusion of Ions through Gases, and the comparison of the numerical solutions show under what conditions the term $\partial n^2/\partial x^2$ can be neglected.

"*Rate of Solution of Hydrogen by Palladium.*" By A. HOLT, D.Sc.

The rate of solution of hydrogen at constant (atmospheric) pressure by palladium in the form of black thin and thick foil has been examined. The rate curves in the case of palladium black are simple and of continuous curvature, but for the foil a more or less pronounced discontinuity of curvature is always observed.

The discontinuity is accounted for by considering that the gas is dissolved in two different forms of the metal, the rate of solution being different in the two forms. Palladium black is believed to consist almost wholly of one form, and hence gives a simple rate curve, whilst the foil (which is mainly crystalline) contains both varieties of metal, and so gives two rates, the first rate passing into the second when solution in both forms becomes equally rapid.

The nature of the two forms of the metal is discussed, and it is concluded that the difference lies in the ordered or haphazard arrangement of the metallic particles.

"*Dispersion of a Light Pulse by a Prism.*" By R. A. HOUSTON, D.Sc.

A light pulse of a form giving the Wien energy distribution is incident on a prism, and expressions are derive

(1) for the disturbance in the region immediately behind the prism where the different colours overlap, and (2) for the disturbance in the focal plane of the telescope. The first expression holds only for a particular law of dispersion, but the second is for any law of dispersion. They are both in accordance with results obtained by Lord Rayleigh by considerations of stationary phase and hydrodynamical analogy, but they go further. For example, it is definitely stated how the amplitude varies in the front and rear of and throughout the train of waves given rise to by the pulse in the different parts of the spectrum.

CHEMICAL SOCIETY.

Ordinary Meeting, March 5, 1914.

Prof. W. H. Perkin, LL.D., F.R.S., President, in the Chair.

(Concluded from p. 141).

65. "*The Influence of Configuration on the Condensation Reactions of Polyhydroxy-compounds. Part I. The Constitution of Mannitoltriacetone.*" By James Colquhoun Irvine and Bina Mary Paterson.

Mannitoltriacetone has been selected as a test substance in an endeavour to correlate the configuration of polyhydroxy-compounds with their capacity to enter into condensation with aldehydes or ketones. It was found that, when dissolved in aqueous alcohol containing minute quantities of hydrogen chloride, the ketonic residues could be removed from mannitoltriacetone in the definite stages indicated below:—

Mannitoltriacetone —> mannitoldiacetone —> mannitolmonoacetone —> mannitol.

Mannitoldiacetone crystallises in needles melting at 37—39°, and has $[\alpha]_D +15.75°$ in alcohol; on methylation it was converted into *dimethylmannitoldiacetone* (b. p. 140—141°/13 mm., $[\alpha]_D +21.9°$), which, on hydrolysis, gave *dimethylmannitol* (needles, m. p. 93°, $[\alpha]_D -8.85°$). This compound, on oxidation with nitric acid, was converted into *dimethylmannonic* acid, which was isolated in the form of the corresponding *lactone* (m. p. 112—114°).

In a parallel series of reactions, *mannitolmonoacetone* (needles, m. p. 85°, $[\alpha]_D$ in alcohol $+23.2°$) was converted into *tetramethylmannitolmonoacetone* (b. p. 138—140°/11 mm., $[\alpha]_D +32.2°$), from which *tetramethylmannitol* was obtained. The compound boiled at 167—169°/13 mm., showed $[\alpha]_D -12.54°$ in alcohol, and gave, on oxidation with nitric acid, a *tetramethylmannonic acid* (b. p. 180—182°/12 mm.) incapable of forming a lactone.

It was also found necessary to examine the form of tetramethylmannitol obtained by the reduction of tetramethylmannose. The compound thus produced boiled at 177°/11 mm., and showed $[\alpha]_D +39.8°$ in alcoholic solution, and is thus isomeric with the product obtained by the hydrolysis of tetramethylmannitolmonoacetone. Moreover, on oxidising tetramethylmannose by means of bromine, a second form of *tetramethylmannonic acid* was isolated, which was readily transformed into *tetramethylmannonolactone* (b. p. 174°/11 mm., $[\alpha]_D +78.8° \rightarrow 38.5°$ in aqueous alcohol.

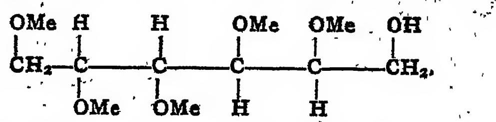
From these results the following conclusions are drawn:—(1) In mannitoltriacetone the ketonic residues are symmetrically linked to α-carbon atoms; (2) the stabilities of the three residues are unequal; (3) the least stable residue is linked to a primary alcoholic group; (4) the most stable residue is linked to the remaining primary alcohol group.

66. "*The Formation of Ethers from Mannitol. An Example of Steric Hindrance.*" By James Colquhoun Irvine and Bina Mary Paterson.

In attempting to prepare mixed ethers by the alkylation of dimethyl- or tetramethyl-mannitol, it was found that the reaction was completely arrested at a stage when a penta-substituted derivative was formed. Thus, 3:4:5:6-tetramethylmannitol, when subjected to the action of silver oxide and ethyl iodide, was converted into the corresponding *tetramethylethylmannitol* (b. p. 140°/8 mm.), and, in a parallel reaction in which methyl iodide was used, the product consisted of *pentamethylmannitol* (b. p. 137—138°/8 mm.). As the latter compound was converted, on oxidation with nitric acid, into a *pentamethylmannonic acid* (b. p. 110°/0.18 mm.), the resistance to methylation was evidently presented by one of the terminal hydroxyl groups.

Notwithstanding the configuration symmetry of mannitol, the remaining primary alcohol group behaved in a different manner, and was readily methylated.

The combined results of the research support the view, expressed in the preceding communication, that the terminal alcohol groups in mannitol preferentially assume fixed positions, with the result that three adjacent hydroxyl groups are arranged on the same side of the carbon chain. Only two of these three groups undergo methylation, and the stereochemical formula of pentametylmannitol is as follows:—



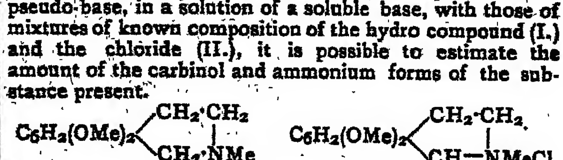
As the silver oxide method of methylation has frequently been employed to discriminate between different types of sugar derivatives, it was necessary to apply the process to 2:3:5:6-tetramethylmannitol in order to ascertain if the secondary alcohol group resisted substitution. The reaction yielded the pentamethylmannitol described above, so that the previous conclusions regarding constitution in the sugar group, which are based on the methylation process, are not affected adversely by the results of the present investigation.

The specific rotations of the partially methylated mannitols now described display a number of regularities from which it is possible to allocate a qualitative rotatory power to each of the four asymmetric systems in mannitol.

67. "*The Relative Strengths of Ammonium and the Substituted Ammonium Hydroxides as Measured by their Action on a Pseudo-base.*" Part I. By Charles Kenneth Tinkler.

The method employed depends on the spectroscopic determination of the amount of the ammonium form of a pseudo-base converted into the corresponding carbinol by the action of a soluble base. 1-Hydroxy-6:7-dimethoxy-2-methyltetrahydro*iso*quinoline has been employed as the pseudo-base.

By comparing the ultra-violet absorption spectra of the pseudo-base, in a solution of a soluble base, with those of mixtures of known composition of the hydro compound (I.) and the chloride (II.), it is possible to estimate the amount of the carbinol and ammonium forms of the substance present.



I. II.

The general result of the investigation is to show that the bases employed increase in strength in the order:—Ammonium hydroxide, trimethylammonium hydroxide, methylammonium hydroxide, dimethylammonium hydroxide, tetramethylammonium hydroxide, which is in accordance with the results obtained by other investigators.

The present investigation has also shown that the conversion of the ammonium form of the pseudo base into the carbinol is in accordance with the law of mass action; that is, concentration of ammonium form of pseudo-base × concentration of hydroxyl ion = K × concentration of carbinol.

68. "*The Interaction between Nitric Acid and Brucine in the presence of Metallic Nitrates.*" By EDWARD HENRY RENNIE and ALFRED ERNEST DAWKINS.

The authors have investigated the effect of metallic nitrates on the interaction between nitric acid and brucine, and have found that the time required to produce a colour of standard depth is very much reduced by the addition of nitrates to the acid. This is in general accord with the results of previous investigations on the effect of nitrates on the interaction betwen nitric acid and copper (*Trans.*, 1908, xciii., 1162; 1911, xcix., 1035).

69. "*Derivatives of 3 : 4-Dimethoxyacetophenone and 4 : 5-Dimethoxy-o tolyl Methyl Ketone: and the Synthesis of Phenylglyoxalines containing Substituents in the Benzene Ring.*" By HENRY STEPHEN and CHARLES WEIZMANN.

The authors have prepared some compounds derived from 3 : 4-dimethoxyacetophenone and 4 : 5-dimethoxy-o-tolyl methyl ketone, and also some new phenylglyoxalines.

4 : 5-*Dimethoxy o-tolyl chloromethyl ketone* melts at 89° and boils at 180°/12 mm.; the corresponding *dihydroxy*-compounds melts at 129° and boils at 187°/12 mm.

Compounds of the type of ω-chloroacetophenones were found on reduction with zinc dust and acetic acid to lead to the formation of acetophenones, with elimination of chlorine.

4 : 5-*Dihydroxy-o-tolyl methyl ketone* melts at 168°.

Phthalimino-3 : 4-dimethoxyacetophenone (compare D.R.-P. 209962), obtained from the corresponding chloroketone by condensation with potassium phthalimide, and by condensation of veratrole with phthaliminoacetyl chloride, melts at 202°.

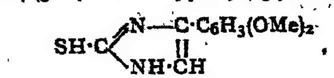
Phthalamino-3 : 4-dimethoxyacetophenone melts at 174°; the amino ketone hydrochloride obtained from this melts at 218° (compare Pictet, *Ber.*, 1909, xlii., 2943).

4 : 5-*Dimethoxy-o-tolyl phthaliminomethyl ketone* melts at 159°, and the *phthalamino* compound at 172°.

4 : 5-*Dimethoxy o-tolyl aminomethyl ketone hydrochloride* melts at 204°, and is similar to the lower homologue.

By condensation of the hydrochlorides of these amino-acetophenones with potassium thiocyanate and potassium selenocyanate (compare Gabriel, *Ber.*, 1894, xxvii., 1037), the following glyoxaline derivatives were prepared :—

2-*Thiol*-4-(3′ : 4′-*dimethoxyphenyl*)-*glyoxaline*,—



melting at 132°, and 2-*thiol*-4(3′ : 4′-*dimethoxy-o-tolyl*)-*glyoxaline*, melting at 155°.

The corresponding *selenomercaptans* melted at 115—117° and 163° respectively.

The above thiol compounds gave the sulphur-free derivatives by oxidation with 10 per cent nitric acid or ethyl nitrite.

70. "*A Delicate Colorimetric Method for Detecting and Estimating Nitrates and Nitrites.*" By EDMUND ALBERT LETTS and FLORENCE WILLIAMSON REA.

The authors have used diphenylbenzidine (Kehrmann, and Micewitz, *Ber.*, 1912, xlv., 2641; Wieland, *Ber.*, 1913, xlvi., 3300; compare also *Bull. Soc. Chim.*, 1914, [4], xv., 186) for detecting and estimating small quantities of nitrates, the test being quite sensitive up to 0·00005 mgrm. of nitric nitrogen, the depth of blue colour depending on :—(1) The temperature, the colour being deeper at higher than at ordinary temperatures; (2) the time that elapses after mixing the nitrate solution with sulphuric acid and diphenylbenzidine; and (3) the amount of nitrate present.

The estimation of nitrates by the new method depends on the depth of the blue tint, and is carried out in small porcelain crucibles. The method may also be employed for estimating both nitrites and nitrates in a mixture of the two.

71. "*The Solubility of the Nitrates of Potassium, Barium, and Strontium, and the Stability of the Double Nitrate of Potassium and Barium.*" By ALEXANDER FINDLAY, IDWAL MORGAN, and IVOR PRYS MORRIS.

The isothermal curves for the system potassium nitrate—barium nitrate—water have been determined at the temperatures 9·1°, 21·1°, and 35·0°, and for the system potassium nitrate—strontium nitrate—water at the temperatures 20·0° and 40·0°. The formation of a double nitrate of potassium and barium was confirmed, and insight into its range of stability acquired. No evidence of the formation of a double nitrate of potassium and strontium was obtained.

72. "*The Azeotropic Mixtures of Ethyl Acetate and Water.*" By RICHARD WILLIAM MERRIMAN.

Wade and Merriman (*Trans.*, 1911, xcix., 997) defined an azeotropic mixture as one which distilled at a constant temperature without change of composition; such a mixture is necessarily one with a maximum or minimum boiling-point. The definition is obviously only applicable to perfectly miscible liquids, but the extension of the term to partly miscible liquids or to non-miscible liquids should not cause confusion. For example, if a mixture of ethyl acetate and water containing 8·43 per cent of water is distilled under a pressure of 760 mm., the boiling-point remains constant at 70·37°, and the distillate contains 8·43 per cent of water at every stage of the distillation The boiling-point is also a minimum to the extent that no other mixture of ethyl acetate and water has a lower boiling-point; but, owing to the fact that this mixture of ethyl acetate and water of constant boiling-point forms two layers right up to the boiling-point, the composition of the mixture in the distilling flask may be varied within wide limits without affecting the boiling-point or the composition of the distillate. (A mixture of any two liquids having two layers right up to the boiling-point must form a mixture of constant boiling-point with a minimum boiling-point, and give a distillate having a constant composition). This fact was clearly pointed out by the author in the original communication (*Trans.*, 1913, ciii., 1797), so that Lattey's criticism (*Proc. Chem. Soc.*, xxx., 33; CHEMICAL NEWS, cix., 117) appears to be unnecessary.

The rest of Lattey's criticism cannot be applied to partly miscible liquids, such as ethyl acetate and water, as the whole of the deductions depend on the use of Duhem's equation, which is applicable only to perfectly miscible liquids.

In the accompanying figure (*loc. cit.*) the region above the line AB is experimentally unrealisable, but the dotted curve below AB is the most probable form of the P/y curve for mixtures of ethyl acetate and water, although mixtures of triethylamine and water give a curve of different shape (Lattey, *Trans.*, 1907, xci., 1965).

Lattey's assertion that the calculation given on p. 1799 of the original communication (*loc. cit.*) is simply an application of Dalton's law of partial pressures, is not strictly true. It is well known that Dalton's law of partial pressures can only be applied to mixtures of saturated vapours when the liquids are absolutely non-miscible (Young, "Stoichiometry," 253, 260).

73. "*Diazotisation of Aminomesitylenes.*" (Preliminary Note). By GILBERT T. MORGAN and JOSEPH REILLY.

Although the study of diazotisation processes is greatly simplified in the mesitylene series by the fact that coupling to form azo-derivatives is prevented by the symmetrical distribution of the three methyl substituents, yet comparatively little attention has been devoted to amino-mesitylenes from this point of view.

Diaminomesitylene is readily converted into either *aminomesitylenediazonium chloride* or *mesitylenebis-diazonium sulphate*; the former salt yields *aminomesitylene-azo-β-naphthol* (bright red needles, m. p. 173°), whilst the latter gives rise to *mesitylenebisazo-β-naphthol* (maroon-red nodules, m. p., indefinite, 270—275°). The

bisazo-derivatives can also be produced by successively diazotising the monoazo-compound and coupling with β-naphthol.

Other diazonium salts illustrating the two stages of diazotisation of diaminomesitylene are under examination, together with the corresponding triazides and the azo-dyes obtained by coupling the mono- and bis-diazonium salts with 2 : 4-tolylenediamine and other bases and phenols.

74. "*The Variable Rotatory Powers of the* d-a-*Bromocamphor-β-sulphonates.*" By William Jackson Pope and John Read.

In applying *d*-*a*-bromocamphor-β-sulphonic acid to the resolution of externally compensated bases, the authors have observed discrepancies amongst the molecular rotatory powers of the salts obtained; they now trace the latter to the occurrence of dynamic isomerism in the acid, and have been able to isolate stereoisomeric ammonium *d*-*a*-bromocamphor-β-sulphonates which exhibit the molecular rotatory powers $[M]_{5461}+271^\circ$ and $+176^\circ$.

75. "*The Optical Activity of Compounds of Simple Molecular Constitution. Ammonium* d- *and* l-*Chloroiodomethanesulphonates.*" By William Jackson Pope and John Read.

The authors have prepared externally compensated chloroiodomethanesulphonic acid, $CHClI{\cdot}SO_3H$, and have resolved it into its optically active components by crystallisation with *d*- and *l*-hydroxyhydrindamine, brucine, and strychnine. Ammonium *d*-chloroiodomethanesulphonate has the molecular rotatory power $[M]_{5461}+43.7^\circ$ in aqueous solution; the optical activity is very persistent, and the salt does not undergo racemisation when its aqueous solution is heated in a sealed tube at 136—150°.

76. "*The Lower Limits of Inflammation of Methane with Mixtures of Oxygen and Nitrogen.*" By Albert Parker.

The lower limits of inflammation of methane have been determined, when mixed with pure oxygen, when mixed with oxygen (80 per cent) and nitrogen (20 per cent), and so on down to an admixed gas containing only 13·5 per cent of oxygen. The mixtures were sparked in a spherical glass vessel of 2·5 litres' capacity, the lower-limit mixture being taken as the one containing the smallest quantity of methane, in which the flame travelled throughout. With pure oxygen, the lower limit of methane is found to be 5·99 per cent, whereas with air the value is only 5·77 per cent. The most probable explanation of the higher value for oxygen is that the specific heat of oxygen is greater than that of nitrogen at the ignition-temperature of methane. A reduction in the oxygen content of the admixed gas from 20 to 13·5 per cent causes an increase in the lower limit of methane to 6·29 per cent.

PHYSICAL SOCIETY.

Ordinary Meeting, March 13, 1914.

Dr. A. Russell, Vice-President, in the Chair.

A paper entitled "*Time Measurements of Magnetic Disturbances and their Interpretation*" was read by Dr. C. Chree.

The paper is a sequel to one read before the Society in November, 1910 (*Proc.*, xxiii., 49), dealing with the times of commencement of fifteen magnetic disturbances discussed by Mr. R. L. Faris, and supposed by him to support Dr. L. A. Bauer's theory that the commencing movements of magnetic storms travel round the globe at rates of the order of 100 km. per second. In his previous paper the author criticised Mr. Faris's paper, and suggested that for an adequate test of Dr. Bauer's theory data could only be obtained from a number of stations encircling the earth. Shortly afterwards Dr. Bauer issued a circular requesting magnetic observatories to send him their measurements of the times of commencement of the fifteen magnetic storms discussed by Mr. Faris. Upwards of thirty stations sent in data in answer to Dr. Bauer's request. A discussion of the data derived from the horizontal force curves has recently been published by Dr. Angenheister, whose conclusions are unfavourable to Dr. Bauer's theory. The present paper deals with the data from the declination and vertical force curves as well as those from the horizontal force curves following a somewhat different method from that adopted by Dr. Angenheister. The bearing of the data on Dr. Bauer's theory is discussed, and the peculiarities of the individual stations are considered.

Discussion.

Prof. S. P. Thompson thought that Dr. Chree's conclusions pointed to the necessity of equipping all magnetic observatories with similar instruments and making them keep records to a tenth of a second.

Mr. R. S. Whipple mentioned the enormous amount of work involved in the reduction of these observations. The instrumental errors due to backlash and other causes were apt to be so great that it was really marvellous that observers went so far as to discuss times of the magnitude involved. He emphasised the need of standardised instruments.

Prof. C. H. Lees said that, like most people who had read Dr. Bauer's paper when it appeared, he had had grave doubts of the instrumental accuracy. He thought the method of calculating the results rather biassed. He had set a student to work out the correlation number of the times of the disturbances and the longitudes of the observatories. The number was too small to justify any conclusion as to connection between the quantities.

Mr. C. W. S. Crawley thought it would be an advantage to work on a much larger time scale, say, 2in. or 3in. per minute, and make use of the little everyday disturbances. He had observed a large number of these in this way. Sometimes the disturbance commenced with a contrary kick and sometimes it did not. The phenomenon, when present, was quite easy to detect. He asked Dr. Chree if no connection ever existed between disturbances and volcanic action.

Dr. A. Russell asked the author if it was known whether atmospheric gales had any effect in producing magnetic storms. It was well known that in the Arctic and Antarctic regions violent magnetic storms were of frequent occurrence. These were often attributed to swarms of electrons flying past the earth. If this were so it would be possible for vortex rings of electric current to be set up which would travel comparatively slowly round the surface of the globe. These might conceivably alter the force components of terrestrial magnetism. In his opinion, the possible effects of the currents existing in the interior of the earth, or set up on its surface by celestial disturbances, ought to be considered as well as the currents in the upper atmosphere.

The Author, in reply, stated that the objection to using a wide time-scale was that an enormous amount of photographic paper would be necessary. Moreover, if the scales are too open, the curves present such a large number of features demanding attention that the staff usually at the disposal of an observatory would be unable to cope with the work involved. The objection to using the small disturbances, which were quite frequent, was the difficulty of ensuring that all the observers were dealing with the same disturbance. Dr. Moos had suggested a connection between certain magnetic disturbances and volcanic action, but he did not think the evidence was conclusive. Dr. Leyst, of Moscow, had established a relation between the amplitude of the ordinary magnetic variations and the height of the barometer.

A paper "*On the Ratio of the Specific Heats of Air, Hydrogen, Carbon Dioxide, and Nitrous Oxide*" was read by H. N. Mercer.

The main object of the experiments was to test the

accuracy with which γ could be measured, employing small quantities of the gas, with the ultimate view of experiments on the variation of γ with temperature. The method employed was to observe with a platinum thermometer of very fine wire the instantaneous fall of temperature corresponding to a given rapid fall of pressure. The method was first employed by Lummer and Pringsheim ("Smithsonian Contributions," 1898), using a bolometer strip, with a vessel of 50 to 100 litres capacity. It was later employed by Makower (*Phil. Mag.*, February, 1903) for the determination of γ for steam, with modifications introduced by Prof. Callendar, which consisted in the substitution of a platinum thermometer, compensated for conduction along the leads, in place of the bolometer strip, and in the adoption of an automatic contact for closing the galvanometer circuit at the right moment, which made it possible to work with smaller quantities of gas. The vessel used by Makower was about 9 litres in capacity. The apparatus employed in the present experiments was similar to that used by Makower, but it was found that with due precautions an equal degree of accuracy was obtainable with a vessel of only 300 cc. capacity.

A table is given in the paper showing the values of the specific heat at constant pressure for the various gases as calculated from the present experiments. The values show good agreement with direct calorimetric determinations.

DISCUSSION.

Prof. C. H. LEES thought the paper marked an advance in the subject. Hydrogen was always a severe test in such measurements, and the corrections were troublesome.

Mr. F. E. SMITH asked what was the diameter of the platinum wire used, as there was probably a lag between its temperature and that of the gas. He thought more information was required on the time of making the galvanometer contact. It was possible that the gas might have commenced to cool, and in consequence to lower the temperature of the thermometer, before the correction due to the heating current had attained its final value.

The AUTHOR stated that the wire was very fine, about a fortieth of a mm. in diameter, and he did not think there could be an appreciable lag.

A paper entitled "*The Asymmetric Distribution of the Secondary Electronic Radiation produced by X-Radiation*," by A. J. PHILPOT, as taken as read.

Homogeneous X-radiations, characteristic of various elements, have been employed to eject electrons from gold. By an ionisation method the relative energies of the electrons emitted in the direction of propagation of the exciting X-radiation and in the reverse direction have been measured for each of the homogeneous X-radiations employed. It has been found that the ratio of the energy of the former to that of the latter increases with the penetrating power of the exciting radiation, its value rising from 1·11, when the mass absorption coefficient of the X-radiation was 5·0, to 1·24, when the mass absorption coefficient was 0·5.

A paper entitled "*A Lecture Experiment on the Irrationality of Dispersion*" was read by Prof. S. P. THOMPSON.

Newton's method of crossed prisms throws an oblique spectrum on the wall. If the prisms used are of identical kinds of glass the oblique spectrum is straight from red to violet. But if different kinds of glass are used, the spectrum is curved by reason of the irrationality of dispersion in one or both of the glasses. If a diffraction grating is used instead of one of the prisms, then the curvature which is observed is that resulting from the irrationality of dispersion of the particular prism employed; and for all known kinds of glass the refraction for blue and violet rays is disproportionately large. To exhibit these effects in the lecture theatre a diffraction grating of 12,000 lines to the inch is employed to cast on the screen a horizontal spectrum of the first order, the light from an arc lamp being sent through a small round or square hole. On interposing a prism to disperse the light vertically upwards, the resultant oblique spectrum is finely curved, being concave upwards. If in the arc lamp the carbons used are those supplied for commercial "flame arcs," the effect is more brilliant, since the spectrum contains several bright bands. If an alloy of zinc, thallium, and lithium is introduced into the crater of the positive carbon, a still more striking series of bright points is produced in the curved spectrum.

SOCIETY OF CHEMICAL INDUSTRY.
(LONDON SECTION).

Ordinary Meeting, March 2, 1914.

Prof. W. R. E. HODGKINSON in the Chair.

THE following papers were read and discussed:—

"*Bleaching of Chemical Pulp and Suggestions for a Standard Method in Test Cases.*" By ARTHUR BAKER and JAMES JENNISON.

The authors have studied the above more particularly from the industrial standpoint and with particular reference to:—

1. Rate of bleaching at constant temperature.
2. Rate of bleaching at varying temperatures.
3. Influence of residual bleach liquors upon the economy of the process.
4. Influence of preliminary acid or alkaline treatment.
5. Influence of the concentration of the pulp.

Conclusions arrived at by observations made during the carrying out of the above experiments are:—

(*a*) That the use of residual bleach liquor or back liquor is attended with an increase in the bleach consumption, and accompanied by a lowering of the colour of the resultant bleach pulp; the use of bleach back liquor only being justified in the washing of material prior to bleaching, when it can be thoroughly removed before the fresh bleach solution is added to the half stuff.

(*b*) That preliminary washing, either by water, dilute acid, or dilute alkali, is not worth while in the case of easy bleaching pulp.

(*c*) That the concentration of the pulp is the most important factor to be taken into consideration, and due regard to this point is absolutely essential in order to obtain the highest economy in the bleaching process as carried out in the paper mill.

(*d*) That a temperature of 120° F. should not be exceeded in any case.

As an outcome of the above experiments, and in view of the fact that Sindall and Bacon's suggestion to use tintometer readings as a method of stating colour values of bleached pulps has not met with any approval, we suggest for arbitration and specification purposes a standard bleaching test on the following lines:—

Minimum quantity of pulp to be taken 10 grms., 10 per cent air dry pulp, 160 cc. of water containing 12 per cent of bleach powder (35 per cent Cl) calculated on the 10 per cent air dry pulp. Temperature, 100° F.; time, two hours.

The pulp is obtained in a fine state of division for bleaching by agitating with a heavily designed brass stirrer of the egg-beater type fitted with teeth.

Samples of the resultant bleached pulp after washing are obtained by making small hand-made sheets, and air drying the same.

For standards of reference, and this has been the main difficulty, we suggest suitable colours be fixed by representatives of the Paper Makers' Association and the Wood Pulp Association. These standards to be official, and matched in dull porcelain as follows:—

A. Colour obtained by first quality easy bleaching sulphite.

B. Colour obtained by second quality easy bleaching sulphite.

C. Colour obtained by first quality easy bleaching sulphate.

D. Colour obtained by second quality easy bleaching sulphate.

Standards to be kept by the Paper Makers' Association and Wood Pulp Association of the various countries as official standards.

The percentage of bleaching powder required to give any of the proposed standard colours would under the conditions of the standard test serve as a direct indication of its value from a white colour point of view.

"*Application of Calcium to the Formation of Alloys.*" By W. R. Hodgkinson.

In connection with copper and some of its alloys a mixture of calcium carbide with borax, boric acid, common salt, or other chlorides was found a very efficient deoxidising flux. A considerable number of metallic oxides, *e.g.*, CaO, ZnO, FeO, PbO_2, are reduced to metal when heated with carbide, but the reagent is not convenient for the purpose. Attempts to reduce oxides of such metals as cerium and zirconium and to form alloys by using a mixture of the metallic oxide, carbide, and copper powder or copper oxide were unsuccessful at ordinary furnace temperatures. Experiments with the chlorides either ready formed or formed *in situ* by introducing a mixture of the oxide and ammonium chloride in small portions at a time into a heated crucible (having regard to the possible volatilisation temperature of the chloride) were more successful.

Two methods for the production of alloys were used. In the former a mixture of halide, carbide, and the principal metal is used, whilst in the latter and better method both or all the metals are as halides. When the former method is used the mixture of dry halide with powdered carbide is dropped on to the principal metal already fused in a crucible, and after the whole is fused the contents are stirred once or twice and poured. When working with mixed halides the mixture with or without an additional flux is placed in a crucible already heated, or packed into the crucible cold and then fused. Much heat is evolved by the interaction of some halides, such as those of copper, lead, zinc, nickel, cobalt, and silver with carbide. This materially assists the reaction when certain of the halides or double salts are simultaneously employed.

Copper has in many cases been used as the principal element of the alloy to be formed. Alloys of this metal, with Co, Ni, Mn, Ce, Zn, Ta, Ti, were formed. The quantities of the four latter metals taken up in the alloy were in all cases less than the theoretical; with the others the loss was not so great; it would probably be less on a large scale.

Alloys of manganese are conveniently formed as the chloride melts without serious volatilisation at below 1000° C. Those containing Bi, Pb, Sn, Sb, Cu, Ag, Co, Ni have been prepared.

Metallographic details are reserved for a later communication.

"*Blasting Gelatin, Some Notes and Theories.*" By W. A. Hargreaves.

Blasting gelatin is officially defined as consisting of nitro-cotton, carefully washed and purified, combined with thoroughly purified nitroglycerin in such proportions that the whole shall be of such character and consistency as not to be liable to liquefaction or exudation, and with or without calcium carbonate or magnesium carbonate not exceeding 2 parts by weight in every 1000 parts of the finished explosive. In actual practice blasting gelatin consists only of nitroglycerin and nitro-cotton.

The author's experience as an inspector of explosives shows that manufacturers have not arrived at a knowledge of a definite proportion of nitro-cotton to use, and have never been certain of producing every time a blasting gelatin complying with the definition already mentioned. With the nitroglycerin there is no trouble, since it is a homogeneous liquid, and one that can be thoroughly washed and purified from all matters liable to confer instability upon it. With nitro-cotton the case is different, there being always the possibility of small particles of impurity remaining in the cotton, surrounded and protected from the washing liquid by the colloidal matter of which the nitro-cotton is composed. Apart from the low-test difficulty there is the more common trouble of exudation of nitroglycerin. For this the usual remedy has been to increase the proportion of nitro-cotton. Four objections are stated to this:—(1) Risk of low-heat test; (2) the blasting gelatin likely to be insensitive to detonation by the ordinary No. 6 detonator; (3) considerable increase in generation of carbon monoxide; and (4) greatly increased cost.

Some years ago an hypothesis was formulated, and has been tested since by observation and experiments. This hypothesis is based upon the theory that blasting gelatin, instead of being a solution of a small quantity of nitro-cotton in a relatively large quantity of nitroglycerin, is really a colloidal solution of a certain quantity of nitroglycerin in nitro-cotton, intimately mixed with some free ungelatinised nitroglycerin.

After discussing this hypothesis the author suggests that the remedy for exudation is not to add more nitro-cotton, but to get a larger amount of gelatinisation during the initial mixing of the nitro cotton and nitroglycerin, and to obtain this end more thoroughness is necessary in the preliminary mixing and also immediate and thorough working in a machine.

ALCHEMICAL SOCIETY.

Roger Bacon.

The eleventh General Meeting of the Alchemical Society was held at the International Club, Regent Street, S.W., on Friday, March 13th. The Chair was occupied by the Acting President, Mr. H. Stanley Redgrove, B.Sc., F.C.S.

A very interesting lecture was delivered by Mr. B. Ralph Rowbottom dealing with the life, thought, and influence of the English alchemist and philosopher, Roger Bacon. After stating that very little was known of the early events in Roger Bacon's life, the lecturer pointed out that two of the factors undoubtedly potent in the formation of his original and pregnant philosophy were his deep knowledge of mathematics acquired during his stay at Oxford, and his study at a slightly later period of the best Arabic writers. The fact was next emphasised that, although Roger Bacon was usually known to us as an alchemist, his great achievement was the creation of a system to be applied in the unravelling of the laws of nature, which was remarkably similar to that we to-day call scientific method. The lecturer proceeded to deal with several of Roger Bacon's works, pointing out the extremely short time in which the most important were written, and he finally gave the construction of the *Opus Majus* in detail. In conclusion, Mr. Rowbottom suggested that the day will probably come when the name of Roger Bacon will no longer call to mind magic or "spooks," but a man who, born into an ignorant age, shed a light not to be considered negligible even in the present century.

The lecture was followed by an animated discussion.

The full text of the lecture and an abstract of the discussion will be published in the March number of the Society's Journal.

Preparation by Catalysis of Decahydroquinoline and Decahydroquinaldine.—Paul Sabatier and M. Murat.—Decahydroquinoline can be prepared by hydrogenation of quinoline over nickel; it is a colourless liquid with a very strong alkaline reaction. An excellent yield of decahydroquinaldine, $C_{10}H_{19}N$, can be obtained by the direct hydrogenation of quinaldine over very active nickel. Like decahydroquinoline it turns red litmus blue, fumes in air, and combines with carbon dioxide, giving a solid carbonate. The authors have also prepared the chloroplatinate, acid oxalate, picrate, &c.—*Comptes Rendus*, clviii., No. 5.

NOTICES OF BOOKS.

The Elements of Qualitative Chemical Analysis. By Julius Stieglitz. Volumes I. and II. London: G. Bell and Sons, Ltd. 1914.

The first volume of this book deals with the fundamental principles of qualitative analysis. Part I. contains a short outline of physical chemistry, which will probably be found sufficiently full for the student who has not already been through a course on the subject. Many references to larger works and to original papers are included, and those which are specially suited for the students' reading are distinguished from the others. The second part explains in detail the application of the general principles to the processes of qualitative analysis. In the second volume a complete course of qualitative analysis is given; this volume is interleaved with blank paper in order that the many questions which are scattered through the text may be answered in writing by the student, who will thus be helping to compile his own text-book. The book is a good example of a thoroughly modern work on qualitative analysis, and provides a valuable training in the scientific method of attacking analytical problems and in careful practical work.

Principles and Practice of Agricultural Analysis. Second Edition. Volume III. *Agricultural Products.* By Harvey W. Wiley, A.M., Ph.D. Easton, Pa.: The Chemical Publishing Co. London: Williams and Norgate. 1914.

The author of this book has made it his special aim to give a succinct account of the historical development of agricultural analysis, and to show clearly the present state of our knowledge of its principles and practice. The book will prove of considerable value as a work of reference, and the copious details it contains will enable the analytical chemist to select and carry out with success any of the methods usually employed in agricultural analysis. Much attention has been paid to continental literature on the subject, and many references are given to foreign periodicals. Special emphasis is laid upon the fundamental principles, and the first part gives a detailed description of general methods and apparatus. Subsequent sections deal with the extraction and identification of the various constituents of vegetable and animal products and the analysis of dairy products and feeding-stuffs, and the determination of nutritive values, &c., are fully treated.

Laboratoriums - Einrichtungen für Quantitative Analyse durch Elektrolyse. ("Laboratory Equipment for Quantitive Analysis by Electrolysis"). Aachen: Gebr. Raacke.

This catalogue of apparatus for the equipment of laboratories for quantitative analysis by electrolysis contains a detailed account of the laboratory of the Königl. Techn. Hochschule at Aachen, which was equipped by Messrs. Raacke, and was the first of its kind in Germany and a model for similar institutions. The catalogue contains an illustrated price list of various kinds of electrical heating and other apparatus.

La Nature des Rayons X. ("The Nature of the X-Rays"). By Augusto Righi. Bologna: Nicola Zanichelli. 1914.

In this lecture, delivered before the Congress of Italian Radiologists at Milan, Prof. Righi described, in the graphic and clear style of which he is a master, recent discoveries relating to the nature of the X-rays. After speaking of the early investigations of the rays, he explained in simple non-technical language the experiments which have been performed on their reflection, and pointed out that the logical conclusion of these experiments is that the X-rays are of the same nature as light rays, and are thus a manifestation of electro-magnetic waves propagated in the ether.

Lectures on the Research Chemist in the Works, with Special Reference to the Textile Industry. By W. P. Dreaper. London: The Institute of Chemistry of Great Britain and Ireland. 1914.

The two lectures contained in this book were delivered before the Institute of Chemistry in October and November, 1913. The lecturer discussed briefly the training required by the research chemist occupied in the textile industries, and the probable nature of the original work which he would be called upon to do. The equipment of the laboratory and the establishment of experimental works are considered, and some special problems are discussed to illustrate the general remarks. Many processes which are employed in the textile industries, such as embossing, waterproofing, silk weighting, &c., are treated, and research chemists, both those who are just entering upon their career and those who have had some years of experience, will find the lectures stimulating and interesting.

Tabellen zur Berechnung der "Theoretischen" Molrefraktionen Organischer Verbindungen. ("Tables for the Calculation of the 'Theoretical' Molar Refractions of Organic Compounds"). By K. v. Auwers and A. Boennecke. Berlin: Julius Springer. 1914.

This handbook is issued as a supplement to Roth and Eisenlohr's book on refractrometery, and is designed to save the worker the lengthy and tedious calculations necessary for obtaining the values of molar refraction and dispersion. The tables include the hydrocarbons, substances containing oxygen and halogen derivatives, and they can also be used for any other elements if the atomic refractions of the latter are known. Only compounds containing up to 15 atoms of carbon are included, and no triple bond derivatives. In the calculations Eisenlohr's four-figure tables of atomic refraction have been used, except in the case of bromine, when results which are probably more accurate have been employed.

International Rubber Congress and Exhibition, Batavia (Java), 1914. Guide to Visitors.

This guide for visitors to the International Rubber Congress and Exhibition to be held at Batavia in September and October, 1914, contains much information relating to the Congress, including the titles of the lectures which will be given and the subjects which will be discussed. Many excursions to well-known rubber estates in West Java and elsewhere will be organised, and the attractions of the island combined with the interesting programme arranged will no doubt induce many experts and others interested in the preparation or cultivation of rubber to attend the Congress.

Sulphurous Anhydride and Camphor.—I. Bellucci and L. Grassi.—It has long been known that camphor readily absorbs large quantities of sulphur dioxide, giving a colourless liquid, which, when left in air, slowly evolves SO_2, and leaves the original camphor behind as residue. The determination of the melting-points of mixtures of the two substances in varying proportions indicates the formation of two compounds, namely, $2SO_2.C_{10}H_{16}O$ (m. p. $-45°$) and $SO_2.C_{10}H_{16}O$ (m. p. $-24°$). The well-known fact that sulphuryl chloride is readily formed by the action of chlorine on SO_2 in presence of camphor is probably connected with the formation of these compounds.—*Atti della Reale Accad. dei Lincei*, xxii., [ii.], No. 12.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clviii., No. 6, February 9, 1914.

Velocity of Reaction in Catalytic Hydrogenations in presence of Platinum Black.—G. Vavon.—The velocity curves of the hydrogenations of substances capable of fixing several molecules of hydrogen show a very different appearance according to the quality and quantity of the catalyst. By heating platinum black its activity may be diminished, so that it becomes unable to effect difficult hydrogenations, while it may still easily catalyse less difficult hydrogenations.

Berichte der Deutschen Chemischen Gesellschaft. Vol. xlvii., No. 2, 1914.

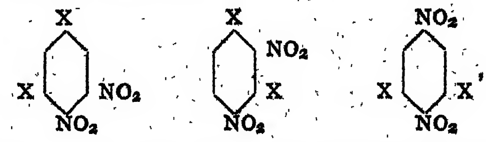
Synthetic Rubber from Isoprene.—G. Steimmig.—Harries has stated that the synthetic rubber prepared from isoprene by heating, and also by acetic acid polymerisation, is chemically identical with para rubber, there being no differences in the derivatives of the two substances. Both are supposed to be composed of the same hydrocarbon, 1.5-dimethyl-cyclooctadiene-1.5. Similar polymerisation products of isoprene have been obtained by heating it in presence of ozonides or peroxides, or by acting upon it with sodium in presence of carbon dioxide. These products yield ozonides from the decomposition of which succinic acid and acetyl acetone result. These two decomposition products must be formed from 1.6-dimethyl-cyclo-octadiene-1.5, and thus rubber prepared artificially from isoprene must consist of a mixture of 1.5- and 1.6-dimethyloctadiene-1.5. The product obtained by Harries gives a similar result. The formation of these two isomeric rings is clearly caused by the asymmetrical structure of isoprene. Natural rubber gives no derivative of 1.6-dimethylcyclooctadiene-1.5, and is thus a single substance. This explains why all rubber-like products artificially obtained from isoprene are not identical in properties with natural rubber.

Tungsten Cyanide.—Arthur Rosenheim and Eitel Dehn.—The authors have prepared a cadmium-triammin salt of the tungsten cyanide anion, $[Cd(NH_3)_3]_2[W(CN)_8].2H_2O$, analogous to the cyanide of molybdenum, $K_4Mo(CN)_8.2H_2O$. They have shown by titration with permanganate that in this compound tungsten behaves like a pentavalent element, and it is thus, like molybdenum, an exception to the valency rule.

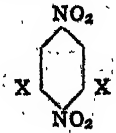
Atti della Reale Accademia dei Lincei. Vol. xxii. [ii.], No. 12, 1913.

Reduction of Aldehydes to α-Glycols.—R. Ciusa and A. Milani.—When aldehyde is treated with magnesium amalgam three different reactions may occur:—(*a*) Reduction to primary alcohol. (*b*) Reduction to disecondary α-glycol. (*c*) Condensation to aldol and subsequent reduction to β-glycol. These reactions proceed with different velocities, and the relative quantities of the products depend upon the velocities. In the case of the aldehydes of the fatty series the last reaction occurs most rapidly, and the β-glycol is the principal product. To prepare 2-4-butylenic glycol an ethereal solution of acetic aldehyde is made, and 2 per cent magnesium amalgam is added in very small portions. The ethereal solution is acidified with dilute sulphuric acid, washed, dried, and distilled. The portion coming over between 180° and 190° is redistilled, when the pure glycol passes over at 184—186°. Propionic and benzoic aldehydes may be treated similarly.

Dinitro Derivatives of Meta-dihalogen Benzenes.—G. Körner and Dr. Contardi.—The authors have extended their study of the dinitro derivatives of meta-dihalogen benzene by preparing and investigating the properties of the following:—



where X is a halogen. They have also obtained dinitro bromo-chloro, chloroiodo, and bromo-iodo derivatives of formula—



Vol. xxiii. [i.], No. 1, 1914.

Distillation of Nitroglycerin at a Low Temperature.—D. Chiaraviglio and O. M. Corbino.—The authors have devised an apparatus in which nitroglycerin can be distilled at a low temperature. By means of this apparatus they found it possible to distil about 10 grms. between 25° and 0°, the operation lasting about forty-four hours. From the data obtained the vapour pressure at 25° could be calculated from the formula $p = \sqrt{\frac{2\pi RT}{M}}m$, where R is the gas constant, T the absolute temperature, M the molecular weight, and *m* the quantity of the substance.

MEETINGS FOR THE WEEK.

Monday, 30th.—Royal Society of Arts, 8. (Howard Lecture). "Surface Combustion," by Prof. W. A. Bone, F.R.S.

Tuesday, 31st.—Royal Institution, 3. "Landscape and Natural Objects in Classical Art," by A. H. Smith, M.A.

—— Royal Society of Arts, 4.30. "Oil Resources of the Empire," by Dr. F. Mollwo Perkin.

Wednesday, April 1st.—Royal Society of Arts, 8. "Sarawak," by Her Highness The Ranee of Sarawak.

—— Society of Public Analysts, 8. "Damage caused to Vegetation by Sulphurous and Sulphuric Acids in the Atmosphere," by R. R. Tatlock and R. T. Thomson. "Abnormal Refraction of Milk Serum," by J. McCrae. "Water of Dorton Spa," by C. A. Mitchell.

Thursday, 2nd.—Royal Institution, 3. "The Progress of Modern Eugenics," by C. W. Saleeby, M.D., &c.

—— Royal Society, 4.30. (Bakerian Lecture). "Series Lines in Spark Spectra," by Prof. A. Fowler, F.R.S.

—— Chemical, 8.30. "The System: Ethyl Ether—Water—Potassium Iodide—Mercuric Iodide; Part III., Solutions Unsaturated with Respect to Solid Phases in the Four component System," by A. C. Dunningham. "Velocity of Saponification of Acyl Derivatives of Phenols—Part I., Velocity of Saponification of Phenyl Benzoate," by H. McCombie and H. A. Scarborough. "General Method for the Preparation of Glyoxals and their Acetals," by H. D. Dakin and H. W. Dudley. "Action of Sulphuric Acid on *p*-Formaldehyde," by J. G. M. Dunlop. "Constitution of the Glycerylphosphates — Synthesis of α- and β-Glycerylphosphates," by H. King and F. L. Pyman. "Destructive Distillation of Soil," by E. J. Holmyard. "Addition Products of Nitrocompounds and Amines," by H. Housley. "Dibenzoylglucoxylose, $C_{11}H_{18}O_{10}(CO{\cdot}C_6H_5)_2H_2O$—A Natural Benzoyl Derivative of a New Disaccharide," by F. B. Power and A. H. Salway.

Friday, 3rd.—Royal Institution, 9. "Further Researches on Positive Rays," by Prof. Sir J. J. Thomson, F.R.S.

Saturday, 4th.—Royal Institution, 3. "Recent Discoveries in Physical Science," by Prof. Sir J. J. Thomson, O.M., F.R.S.

THE CHEMICAL NEWS.

VOL. CIX., No. 2836.

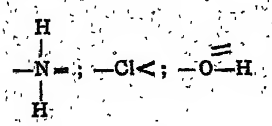
AN ENQUIRY INTO THE CONSTITUTION OF THE BENZENE NUCLEUS WITH REFERENCE TO THE PHENOMENON OF DI-SUBSTITUTION.

By CECIL L. HORTON.

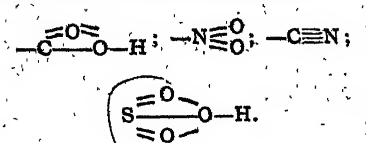
THE rule governing di-substitution is usually referred to as Crum Brown's rule, and reads—"If monosubstituent A is such that HA can be readily oxidised to HO.A the di-compound will be *meta*; otherwise *p* and *o*. Generally in the latter case *p* predominates." A list of the commoner radicles is given below in the appropriate column:—

o and *p*.	*m*.
NH_2	$C{=}O$ / $C{-}OH$
$NH{-}$	NO_2
$-OH$	CN
Cl	SO_3H
Br	
I	

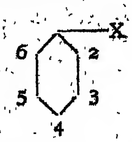
It will be noticed that each of the radicles in the first column is unsaturated:—



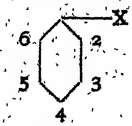
while those in the *m* column are saturated:—



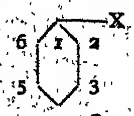
The effect of an unsaturated group displacing a hydrogen in the nucleus is to alter the distribution of the valency thus:—More of the valency of C_1 is absorbed by X leaving C_2 with an excess, which in turn takes more than its usual share from C_3. In C_4, owing to the shortage on C_3, has an excess. C_2 and C_4 will be more reactive than C_3. "Steric hindrance" will account for the predominance of the *p* di-substituted compound over the *o*.



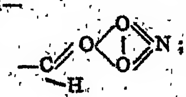
In the case of a saturated group it is extremely improbable that the distribution of the valency of the carbon at the junction is the same in the case of such a group as in the case of hydrogen. The heavily saturated element probably has only a minimum valency free to bind it to the carbon, and, therefore, the carbon to which the group is attached has more than the usal amount of valency to distribute to C_2 and C_6, and hence the valency of C_2 is distributed unevenly between C_1 and C_3, the smaller amount going to C_3. The same applies to C_6 and C_5. C_3 and C_5 have valency which cannot be entirely satisfied, by C_4, and hence the *m* position is the reactive one.



With regard to the behaviour of methyl, ethyl, &c. benzene, which compounds, while possessing as apparently saturated side chain, yet fall in the first of the groups mentioned, the following explanation is offered. Werner accounts for the existence of triphenyl-methyl on the grounds that C_6H_5 absorbs more of the carbon valency than does H, and therefore $(C_6H_5)_3C$ is less saturated than is CH_3. Applying this principle we have that the carbon to which the alkyl group is attached has less than normal amount for C_2 and C_6, *i.e.*, it behaves as if the alkyl group were unsaturated, since it gives more than the usual share to the carbon in the side chain.



Side chains of the type $C{\lessgtr}^{O}_{H}$, *i.e.*, aldehydes and aromatic ketones, behave in an exceptional fashion. The radicle is essentially unsaturated, and yet the compounds formed by direct nitration are of the meta variety. Such an occurrence is best explained on the basis of an intermediate compound—



the radicle is thus saturated, and the NO_2 migrates to the meta position.

RELATIONS BETWEEN THE ROTATORY POWERS OF THE MEMBERS OF HOMOLOGOUS SERIES.*

By ROBERT HOWSON PICKARD and JOSEPH KENYON.

ATTEMPTS to discover a connection between the rotatory power and chemical constitution of a compound have been numerous since Crum Brown and Guye independently, in 1890, brought forward the theory connecting mass and molecular rotatory power. This now discarded theory has stimulated a large amount of research, the results of which up to 1904 have been summarised by Walden (*Ber.*, 1905, xxxviii., 345) and since then up to 1912 by Frankland (*Journ. Chem. Soc.*, 1912, ci., 654). The comparative failure (as regards the solution of the problem under consideration) of all this painstaking and laborious work led the present authors to plan a fresh investigation of the problem. Their results are as yet very incomplete, and have so far yielded no definite solution of the problem, but are put forward as a basis of discussion, as they appear to indicate some (at least) of the causes of the comparative failure of the earlier investigations. (See *Journ. Chem. Soc.*, 1911, xcix., 45; 1912, ci., 620 and 1427; 1913, ciii., 1923; 1914, cv., 94; *Proc. Chem. Soc.*, 1912, xxviii., 42; 1913, xxix., 296; *Ber.*, 1912, xlv., 1592.)

Previous investigators have studied as a rule the effect of various substituents on the rotatory power of some *one* optically active compound—in the great majority of cases,

* A Contribution to a General Discussion on "Optical Rotatory Power," held before the Faraday Society, March 27, 1914.

the effect of substituting the alcoholic or carboxylic hydrogen atoms in tartaric, glyceric, and malic acids and in borneol and menthol. It is highly significant, in view of some of our later results, that, almost without exception, the homologous series mentioned in the two summaries quoted above are all composed of esters, a class of compounds which it would now appear are particularly prone to exhibit *anomalous* rotatory dispersion. To this, and to the once universal custom of determining the rotatory power for sodium light only, as well as to the very frequent disregard of the effects of temperature and even of solvents, a great deal of the present confusion in the interpretation of the older results is most probably due.

When planning a reinvestigation of this problem, the authors determined to synthesise and examine optically active compounds of the simplest possible chemical constitution, each containing only one asymmetric carbon atom and, as far as possible, having the various radicles (the effect of which on the rotatory power was to be studied) attached directly to it. At first it appeared desirable to restrict the investigation to the examination at different temperatures of homogeneous liquids, but it has since been found that some well-marked relations (due solely to the molecular configuration) which exist between the rotatory powers of the members of some series could only be observed in solution, as they are masked at all temperatures up to the boiling-point when the compounds are examined in the homogeneous state.

So far there have been synthesised and systematically examined about forty secondary alcohols and some ninety esters derived from them. These are all of the general formulæ $R_1 \cdot CH(OH) \cdot R_2$ and $R_1 \cdot CH(O \cdot CO \cdot R_3) \cdot R_2$, respectively, where R_1, R_2, R_3 are normal alkyl radicles and comprise the following eleven homologous series of optically active compounds:—

i. The carbinols of the series $CH_3 \cdot CH(OH) \cdot R$, hereafter called the "methyl" series.
ii. The acetates of these carbinols, $CH_3 \cdot CH(O \cdot COCH_3) \cdot R$.
iii. The dodecoates of the same, $CH_3 \cdot CH(O \cdot COC_{11}H_{23}) \cdot R$.
iv. The esters of butan-β-ol, $CH_3 \cdot CH(O \cdot COR) \cdot C_2H_5$.
v. The esters of pentan-β-ol, $CH_3 \cdot CH(O \cdot COR) \cdot C_3H_7$.
vi. The esters of hexan-β-ol, $CH_3 \cdot CH(O \cdot COR) \cdot C_4H_9$.
vii. The esters of heptan-β-ol, $CH_3 \cdot CH(O \cdot COR) \cdot C_5H_{11}$.
viii. The esters of octan-β-ol, $CH_3 \cdot CH(O \cdot COR) C_6H_{13}$.
ix. The esters of undecan-β-ol, $CH_3 \cdot CH(O \cdot COR) C_9H_{19}$.
x. The carbinols of the series $C_2H_5 \cdot CH(OH) \cdot R$, hereafter called the "ethyl" series.
xi. The carbinols of the series $(CH_3)_2CH \cdot CH(OH) \cdot R$, hereafter called the "*iso*propyl" series.

Each of the compounds comprising these series contains only one asymmetric carbon atom and is of the simplest possible chemical constitution, this latter being moreover similar for all the compounds.

The relation between the rotatory powers of the members of these series can be readily explained in a qualitative sense by a consideration of the size of (or space occupied by) the radicles attached to the asymmetric carbon atom. Thus, representing the compounds by the symbols $C\,a\,b\,c\,d$, the effect of increasing the size of d (representing the "growing chain" in a series) is to alter in a more or less regular manner (usually to increase) the molecular rotatory power of the compounds. In the "methyl" series the space occupied by a, b, and c is the smallest conceivable (CH_3, H, OH), and the values of the molecular rotatory power when measured in the homogeneous state increase regularly by small increments as the chain grows. In solution (ethyl alcohol and benzene), however, the rotatory powers of individual members of the series are considerably exalted when the whole molecule itself approximates in configuration to a ring structure, as in pentan-β-ol and decan-β-ol, or when the growing chain in a similar manner all but returns on itself, as in methyl amyl carbinol (heptan-β-ol) and methyl decyl carbinol (dodecan-β-ol). When, however, the space occupied by the groups or atoms represented by a, b, and c is larger, the increase in molecular rotatory power, as d increases, becomes less regular. Either (1) it may be specially affected when the chain returns on itself, as in the "ethyl" series, where ethyl amyl, ethyl decyl, and probably ethyl pentadecyl carbinols (both in the homogeneous state and in solution) have values for the molecular rotatory power which are above those of the immediately preceding and succeeding members of the series, or (2) the increase may be relatively large until the growing chain d contains five carbon atoms with an increase of a much smaller order in the molecular rotatory power of successive members. This, for example, occurs in all the series of esters (except Nos. ii. and iii.) mentioned above, in which there is a rapid increase in the value of the molecular rotatory power $[M]_D$ 20° for each member of the series up to the valerate, and a still further, but relatively much smaller, increase for each member from the valerate to the stearate when these are examined in the homogeneous state at 20°. When, however, the space occupied by the groups a, b, and c is still greater, the "approximate maximum" is reached when the growing chain contains fewer than five carbon atoms. Thus in the series of dodecoates, where the group $—O\,CO \cdot C_{11}H_{23}$ is large, the molecular rotatory powers increase in value rapidly up to that for $C_4H_9 \cdot CH(O \cdot COC_{11}H_{33})CH_3$ with a much smaller increment beyond. Results of a similar character have been observed in the "*iso*propyl" series of carbinols. When examined in the homogeneous state, the member containing four carbon atoms in the growing chain has the conspicuous value for the molecular rotatory power; on the other hand, in ethyl-alcoholic solution it is the member containing five carbon atoms in the growing chain which has the conspicuous value.

In the series of acetates particularly instructive results have been obtained. Here the grouping $—O \cdot CO \cdot CH_3$ is the smallest of the corresponding groups in the compounds examined, and it is found that the values of $[M]$ 20° decrease rapidly in the series until the member $C_6H_{13} \cdot CH(O \cdot CO \cdot CH_3) \cdot CH_3$ is reached, after which the rate of decrease becomes very much smaller. It should, however, be noted that in all the series of esters the growing chain $—CO \cdot R$ is attached only indirectly to the asymmetric carbon atom by means of another oxygen atom.

By including the examination of these esters in the investigation, the authors' original plan has been abandoned, but this is justified as the optical rotatory dispersions of the esters in general offer such a striking contrast to those of the carbinols. Thus for the latter it has been observed that (1) in an homologous series the rotatory dispersion ratio becomes constant (within the limits of experimental error) as soon as the growing chain has become distinctly the largest group attached to the asymmetric carbon atom, and (2) the value of the ratio for a given carbinol is constant between wide temperature limits (20° to 200°), whereas for the esters (except perhaps for some of the β-butyl esters) these generalisations do not hold.

The rotatory powers of the esters as a rule are decreased (often to the extent of changing the optical sign) by solvents and by increase of temperature, the depressing effect for each set of conditions being a similar one for each of the different series. By suitable choice of conditions either of temperature or of concentration in some such solvents as carbon bisulphide, pyridine, or benzene, the esters can be *caused* to exhibit anomalous rotatory dispersion. These conditions must be such that the $[\alpha]_D$ of the d ester is depressed so that it lies between $+2 \cdot 5°$ and $\pm 0°$. It has been shown above how in a qualitative sense the relations between the molecular rotatory powers of the esters when measured at 20° in the homogeneous state can be explained, but such explanation would probably have been impossible had the temperature at which the comparisons were made been selected at above 150° when so many of the esters exhibit anomalous dispersion.

The results appear to be due to alterations in the complexity of the molecules and can be co-ordinated on the

assumption that each ester is a mixture of two isomers, which have rotatory powers of opposite sign and different dispersive power. Such co-ordination is effectively brought out by the construction of "characteristic diagrams" drawn in the manner described by Armstrong and Walker (*Proc. Roy. Soc.*, 1913, A, lxxxviii., 388).

The present authors therefore suggest that (1) in general two forms of any one ester can exist; (2) the proportion of these two forms present varies according to the conditions of temperature or solution; (3) the difference is due to the exercise of the supplementary valency of the oxygen atom in one of the forms, and (4) when the two forms differ in dispersive power and optical sign, anomalous dispersion may be observed. In an homologous series of esters the effect of the growing chain on the rotatory powers of the two isomers (supposed to be present) would be likely to vary in a more or less regular manner throughout the series. In the series of esters mentioned above, since the region in which anomalous dispersion has been observed lies near to $\pm 0^\circ$, the dispersive powers of the isomers cannot be very widely different in the case of any of the compounds, whilst if there be any connection at all between chemical constitution and rotatory power the values of the rotatory power of the various esters should bear some relationship, as all the radicles are alike. No numerical relation has so far been observed—it is not yet possible to choose a set of conditions suitable for instituting comparisons—but it is significant that the *same* characteristic diagram appears to correlate all the determinations of the rotatory power of one of the optical antipodes of the compounds comprising the eleven series mentioned above, in addition to other derivatives of the carbinols themselves.

In this respect the properties of *l*-methyl α-naphthyl carbinol are very instructive. It melts at 47°, but will remain in the supercooled state, and at 10° it has $[\alpha]_{\mathrm{Hg\ violet}}$ $-8\cdot0^\circ$, showing at and within a few degrees of this temperature anomalous dispersion; at 120° it has $[\alpha]_{\mathrm{Hg\ violet}}$ $-77\cdot4^\circ$, at and above which temperature the dispersion remains approximately constant. In 5 per cent carbon bisulphide solution it has $[\alpha]_{\mathrm{Hg\ violet}}$ $-198\cdot9^\circ$, whilst it forms a dextro-rotatory hydrogen phthalic ester, which in 5 per cent ethyl alcoholic solution has $[\alpha]_{\mathrm{Hg\ violet}}$ $+171\cdot7^\circ$. These determinations range over 370° and can be correlated on *one* characteristic diagram. It can be assumed here that (1) two forms of the carbinol with different dispersive power and of opposite optical sign exist, owing to different dispositions of the valencies in the naphthyl radicle; and (2) the rotatory powers of these two forms and their esters are *principally* determined by the groups attached to the asymmetric carbon atom.

At least it seems now capable of proof that the rotatory power of a derivative of a given optically active compound *is* some function of the rotatory power of the latter, although the highly constitutive character of this physical property makes the problem still one of extreme complexity.

Specific Heats and Heats of Fusion of the Alkaline Metals.—E. Rengade.—The atomic specific heat of the alkaline metals, although always approximately 6, increases regularly with the atomic weight, while the atomic heat of fusion regularly decreases. The ratio of the atomic heat of fusion to the absolute temperature of fusion is a number which is nearly constant for all the four metals investigated; the difference between the extreme numbers (for potassium and cæsium) does not exceed 2·5 per cent. If the variation of the specific heats with the temperature is investigated it is found that for the solid metals the temperature coefficient increases rapidly for rubidium and cæsium. With the liquid metals the reverse is the case.—*Bull. Soc. Chim. de France*, xv.-xvi., No. 4.

THE RELATIVE ABUNDANCE OF SEVERAL METALLIC ELEMENTS.

By F. W. CLARKE and GEORGE STEIGER.

DURING the past twenty-five years several estimates of the relative abundance of the commoner chemical elements have been published from the laboratory of the United States Geological Survey. (For the latest of these estimates see *Bulletins* 419 and 491, U.S. Geol. Survey; also a paper in *Proc. Am. Phil. Soc.*, li., 214). These estimates, however, covered only such constituents of the earth's crust as are usually determined in the course of fairly complete analyses, including, in many cases, the less important elements barium, strontium, nickel, chromium, vanadium, and zirconium. For the more familiar metals, copper, lead, zinc, and arsenic, no really adequate data were available, and no attempt was made to compute either their abundance or their frequency. Such attempts have been made by others, however, but not altogether conclusively. (See, for example, Vogt, *Zeit. Prakt. Geol.*, 1898, pp. 225, 314, 377, 413, and 1899, pp. 10, 274; and Kemp, "Econ. Geol.," i., 207).

In order to gain a definite idea as to the relative abundance of the elements in question, a number of *composite* analyses were made. That is, in each group of substances investigated, many samples were blended into one uniform sample, and that was then analysed. The average content of each metal was determined in that way with as close an approximation to accuracy as could have been attained by many individual analyses. Four such composites have been studied thus far; namely, two of oceanic clays, contributed by Sir John Murray (for the complete analyses of these clays see *Journ. Geol.*, xv., 783); one of silt or mud from the delta of the Mississippi; and one of igneous rocks which had previously been analysed in the laboratory of the Survey. For the Mississippi silt the general analysis, not heretofore published, is as follows:—

TABLE I.—*Composite Analysis of 235 Samples of Mississippi Silt.*

SiO_2	69·96
Al_2O_3	10·52
Fe_2O_3	3·47
MgO	1·41
CaO	2·17
Na_2O	1·51
K_2O	2·30
H_2O-	3·78
H_2O+	1·96
TiO_2	0·54
ZrO_2	0·05
CO_2	1·40
P_2O_5	0·18
SO_3	0·03
S	0·07
Cl	0·30
F	0·07
Cr_2O_3	0·01
V_2O_3	0·02
NiO	0·017
MnO	0·06
BaO	0·08
SrO	Trace
CuO	0·0043
ZnO	0·0010
As_2O_5	0·0004
PbO	0·0002
Organic	0·66
	100·6229
Less O	0·13
	100·4929

(Note.—Except when otherwise stated the analyses given here were made by Mr. Steiger).

The composite was made up of 235 separate samples, collected by E. W. Shaw. For the determination of NiO, CuO, PbO, ZnO, and As_2O_5, 200 grms. of the silt were taken. The presence of organic matter prevented the separate determination of ferrous iron. The chlorine in this analysis is doubtless due to salt from the Gulf of Mexico.

For the four composite analyses above mentioned the data under immediate consideration are as follows:—

A. The "red clay" of the oceanic depths. Composite of 51 samples dredged from the sea bottom and representative of all the great oceans. The larger part of this material was collected by the *Challenger* Expedition. Determinations (by E. C. Sullivan) of CuO, ZnO, PbO, and As_2O_5 made on 150 grm. portions.

B. "Terrigenous clays," from oceanic depths of 140 to 2120 fathoms. Composite of 52 samples, namely, 4 "green muds" and 48 "blue muds," also mainly from the *Challenger* Expedition. Determinations made on 300 grm. portions.

C. Composite of 235 samples of Mississippi silt, as in the foregoing analysis. For the heavy metals 200 grm. portions were taken.

D. Composite of 329 igneous rocks, all American. Determinations on 90 grm. portions.

In the red clay a trace of molybdenum was also detected by Dr. Hillebrand.

Table II.—*Summary of Data from Composite Analyses.*

	A.	B.	C.	D.	Average.
NiO ..	0·0320	0·0630	0·0170	0·00655	0·0296
As_2O_5 ..	0·0010	Trace	0·0004	0·00074	0·0005
PbO ..	0·0073	0·0004	0·0002	0·00081	0·0022
CuO ..	0·0200	0·0160	0·0043	0·01167	0·0130
ZnO ..	0·0052	0·0070	0·0010	0·00638	0·0049

These figures give quite clearly the order of magnitude of the several percentages, and they are corroborated by the work of other investigators. In a series of 36 igneous and metamorphic rocks of British Guiana, Harrison found a mean percentage of 0·025 copper. In 23 of his samples lead was also sought for, and detected in 5 of them, the maximum amount being 0·02 per cent. In a typical specimen of the Columbia River basalt Wells found 0·034 of copper, and the same quantity was determined by Jensen in an andesite from Fiji. In the porphyries of Leadville, Colorado, Hillebrand was able to determine lead. Out of 18 samples, taken at points remote from ore bodies, the average amount found was 0·002 per cent of PbO. One porphyry also yielded 0·008 per cent of zinc oxide, and a rhyolite contained 0·0043 per cent.

In four rocks, granite, porphyry, and diabase from the Archean of Missouri, Robertson determined the following percentages of lead, zinc, and copper:—

Pb	0·00197 to 0·0068;	average, 0·004
Zn	0·00139 to 0·0176;	average, 0·009
Cu	0·00240 to 0·0104;	average, 0·006

The adjacent limestones also carried these metals, but in slightly smaller proportions. Similar results were obtained by Finlayson from igneous rocks adjacent to lead mines in Great Britain. His averages are—Pb 0·0032 per cent, and Zn 0·028. In the lime stones and dolomites of the Dubuque region, Iowa, Weems determined lead and zinc. The average of 9 samples gave 0·00326 per cent of Pb, and 0·00029 of Zn. Many other determinations of the heavy metals in rocks are scattered through the literature of geology, but these examples are sufficient to illustrate what has long been known. The researches of Forchhammer, of Sandberger, and of Dieulafait are familiar to geologists, but they lack the quantitative basis which is supplied by the composite analyses given here. (For literature references see *Bulletin* 491 U.S. Geol. Survey; "The Data of Geochemistry," pp. 600—602, 643). The heavy metals are widely diffused throughout the crust of the earth, and generally in determinable proportions. The order of abundance, as now ascertained, appears to be Ni, Cu, Zn, Pb, As, with, of course, local variations.

With the aid of the estimate here given for zinc, which is near 0·005 per cent of ZnO or 0·004 Zn, it becomes possible to gain some notion as to the relative abundance of cadmium; for the two metals are commonly associated. In 10,906 shipments of zinc ores from Webb City and Joplin, Missouri, mostly in carload lots, Waring found an average percentage of 57·96 Zn and 0·358 Cd. (Cited by Siebenthal in U.S. Geol. Survey, "Mineral Resources," 1908, i., 796; see also, for other data, Waring's paper in *Journ. Am. Chem. Soc.*, xxvi., 16). The ratio is 1 Cd to 162 Zn. From 42 analyses of sphalerite given in Hintze's "Handbuch der Mineralogie," the mean ratio is 1 to 163. From 82 analyses of European zinc ores, cited by Jensch, the ratio 1 to 277 appears (Ahren's "Sammlung Chem. Tech. Vorträge," iii., 201). The mean of these three estimates is 1 to 201; that is, in round numbers, zinc seems to be about 200 times as abundant as cadmium. A more precise estimate can hardly be made at present; but the figure is better than no estimate at all. It has a quantitative basis, and is therefore something more than a mere guess. If the percentage of zinc in the earth's crust is 0·004, then that of cadmium is of the order of 0·00002.

In the course of the regular rock analyses made in the laboratory of the Geological Survey, many determinations have been made of elements of minor quantitative importance. These determinations are numerous enough to fix their numerical significance between maximum and minimum limits as follows:—

In round numbers, about 1200 such analyses, nominally complete, have been made, and in 793 of them barium oxide was determined or proved to be absent. The mean of these determinations, counting absences as zero, is 0·104 per cent, which is probably a maximum. If the remaining 407 rocks were all free from barium, and so regarded, the average percentage of BaO would be 0·069, a minimum, and between the two figures the most probable value would lie, their mean being 0·086. Upon this basis of computation the following table of percentages has been constructed:—

Table III.—*Summary of Data from Rock Analyses.*

	Number of determinations.	Maximum.	Minimum.	Mean.
BaO ..	793	0·104	0·069	0·086
SrO ..	649	0·040	0·022	0·031
Li_2O ..	581	0·011	0·005	0·008
NiO ..	299	0·026	0·006	0·016
Cr_2O_3 ..	293	0·050	0·012	0·031
V_2O_3 ..	102	0·026	0·002	0·014
ZrO_2 ..	372	0·023	0·007	0·015

In three of the composite analyses already cited, similar determinations were made, and the results obtained fit in fairly well with the figures of this table.

The percentages found are shown in the following table:—

Table IV.—*Data from Analyses of Composite Samples.*

	Red clay.	Terrigenous clay.	River silt.
BaO	0·17	0·05	0·08
SrO	0·046	0·025	Trace
NiO	0·032	0·065	0·017
Cr_2O_3 ..	0·01	0·044	0·01
V_2O_3 ..	0·028	0·028	0·02
ZrO_2 ..	Undet.	Undet.	0·05

The data so far obtained may not be final, but they clearly indicate the several orders of magnitude which it was sought to determine.—*Journal of the Washington Academy of Sciences*, iv., No. 3.

A CORRELATION OF THE ELASTIC BEHAVIOUR OF METALS WITH CERTAIN OF THEIR PHYSICAL CONSTANTS.*

By JOHN JOHNSTON.

As is well known, the effect of pressure acting on both the solid and liquid phase of a single substance is to raise or lower its melting-point according as the process of melting is accompanied by an increase or a decrease of volume respectively, the latter being the exceptional case. But when pressure acts only on the solid phase, but not —or not to the same extent—on the liquid phase, the melting-point is always lowered and by an amount which is many times as great as the corresponding change produced by the same pressure acting on both the liquid and the solid phase. For example, the melting-point of ice is lowered by 0·0075° per atmosphere of equal pressure, but by about twelve times as much, or 0·09° per atmosphere, when the pressure acts only on the ice (see Note 1). The latter type of pressure we shall for convenience in what follows designate by the term "unequal pressure."

A study of the work of Spring and others rendered evident a parallelism between the melting-point of a substance and the ease with which it will, when subjected to (non-uniform) compression, flow or weld into a more or less solid block; namely, that the higher the melting-point of the material the less readily does it flow, or weld together, under compression. From this it is obvious that, if it be assumed that the process of flow is a manifestation of a real melting produced by the compression, the pressure must be unequal in character; that is, the pressure acting on the solid must be greater than that on the liquid phase. For, when the same pressure acts on both phases, the melting-point of practically all substances is raised, and not lowered, as, on this explanation of the phenomenon, we assume it to be. It seemed of interest, therefore, to calculate the effect of unequal pressure in lowering the melting-point of metals, to compute the amount of such pressure required to cause the metal to melt at or about the ordinary temperature, and to investigate if the pressure computed in this way can be correlated with any of the mechanical or other properties of the metals.

The equation made use of in calculating the effect of unequal pressure on the melting-point is derived most readily in the way employed by G. N. Lewis (*Journ. Am. Chem. Soc.*, 1908, xxx., 680) in a parallel case—the calculation of the variation of osmotic pressure with temperature (see Note 2).

Let A be the activity of the substance in the solid phase, and A′ the activity in the liquid phase (see Note 3). Now, if the pressure on the solid phase alone is increased by dP, then the temperature of equilibrium will be changed by an amount dT. Since both phases are initially in equilibrium, the activity of the solid (A) and that of the liquid (A′) must be equal; moreover, they must again be equal when equilibrium is re-established. Hence $A = A'$, and $dA = dA'$, or $d\ln A = d\ln A'$.

Now, the change in $\ln A$ is due to temperature change alone; the change in $\ln A'$ is due to change in temperature and change in pressure; that is—

$$d\ln A = \left(\frac{\partial \ln A}{\partial T}\right) dT$$

and—

$$d\ln A' = \left(\frac{\partial \ln A'}{\partial T}\right) dT + \left(\frac{\partial \ln A'}{\partial P}\right) dP.$$

Equating the right hand members of these equations, we have—

$$\left(\frac{\partial \ln A}{\partial T}\right) dT - \left(\frac{\partial \ln A'}{\partial T}\right) dT = \left(\frac{\partial \ln A'}{\partial P}\right) dP.$$

Substituting for the partial differentials their values from the fundamental thermodynamic equations (see Note 4), and combining the left hand terms, gives—

$$\frac{L\,dT}{RT^2} = \frac{V\,dP}{RT}$$

or—

$$\frac{dT}{dP} = \frac{VT}{L} \quad . \quad . \quad . \quad . \quad . \quad . \quad (I.)$$

where V is the molal volume of the solid phase, T its melting-point on the absolute scale (both phases under the same pressure), and L its molal heat of fusion. The quantities V and T are always positive, but L (as here used) is always negative; hence application of excess pressure on the solid phase always lowers the melting-point (see Note 5).

This differential equation is rigorously correct; but in order to integrate it, we must know how V and L change with the temperature and with the pressure. The variation of V is determined by the coefficients of expansion and of compressibility, which are known for comparatively few substances. With regard to the other factors, our knowknowledge of L at the ordinary melting-point under atmospheric pressure is as yet extremely unsatisfactory in character and limited in scope, while our ignorance of its variation with either temperature or pressure is practically complete. However, in the case of the metals at least, this difficulty is not so serious, as is shown by the following considerations:—

The variation of melting-point with pressure, acting equally on both phases, for all the metals which have so far been investigated, has been found to be practically linear within the error of experiment (see Note 6). It is a necessary consequence of this linearity that with increasing pressure the relation between L and (V – V′) (V′ is the molal volume of the liquid phase) must be linear, or, in the limiting case, remain practically constant. It is, therefore, very plausible that we are justified in assuming that the variation of L with V is linear. Integrating Equation I. on this basis, between the limits T_1 (the ordinary melting-point at 1 atm. pressure, expressed on the absolute scale) and a given temperature θ, we obtain the equation—

$$P = \frac{L}{V} \ln \frac{T_1}{\theta} \quad . \quad . \quad . \quad . \quad . \quad (II.)$$

Instead of the molal values we may substitute the heat of fusion (Q_1) per grm. of substance, and the density (D_1) of the solid, at the ordinary melting-point (T_1) (see Note 7); making the necessary transformations we obtain finally the equation—

$$\phi = 95{\cdot}1 Q_1 D_1 \log \frac{T_1}{\theta}, \quad . \quad . \quad . \quad . \quad (III.)$$

which enables us to calculate the melting pressure (ϕ, expressed in atmospheres) corresponding to the temperature θ; that is, ϕ is the pressure required to cause the substance to melt at the absolute temperature θ.

This formula has been applied to the calculation of the excess pressure (acting on the solid only) required to cause the metal to melt at 27° (that is, $\theta = 300°$) in the case of all the metals for which values of Q are given in "Landolt-Börnstein-Meyerhoffer Tabellen" (2 Aufl., p. 470) (see Note 8). For some metals more than one value is given, but it is at present impracticable to determine which are most reliable; for this reason the mean value was adopted in all such cases. For the same reason the general mean value of the density, as given in the tables (p. 224), was taken. The melting points are those now generally adopted.

The data and results are brought together in Table I., in which the metals are arranged in the order of increasing values of the melting pressure calculated in this way from Equation III. It was conjectured that this order might bear some relation to that obtained when these metals are arranged with reference to the relative values of the elastic constants and mechanical properties.

* From the *Journal of the American Chemical Society*, vol. xxxiv., No. 6.

Table I.—*Lowering of Melting-point of Metals Effected by One Atm. Unequal Pressure, together with the Computed Melting Pressures at Ordinary Temperatures.*

Metal.	Melting-point. t.	Melting-point. T_1.	Heat of fusion. Q.	Density. D.	ΔT_1 (*a*)	ϕ_{27} (*b*)
K	62	335	15·7	0·87	0·59	64
Na	97	370	31·7	0·98	0·29	266
Pb	327	600	5·4	11·37	0·24	1760
Sn	232	505	14·1	7·29	0·12	2200
Bi	270	543	12·5	9·80	0·11	3000
Cd	321	594	13·7	8·64	0·12	3300
Al	658	931	42·0	2·60	0·21	5100
Zn	419	692	28·0	7·1	0·084	6900
Ag	960	1233	23·0	10·50	0·12	14000
Cu	1083	1356	43·0	8·93	0·086	24000
Pd	1550	1823	36·3	11·4	0·11	31000
Pt	1755	2028	26·2	21·5	0·084	46000

(*a*) This column, which represents the melting-point depression produced by 1 atm. excess pressure acting on the solid, is added merely to give an idea of the magnitude of this quantity. The values given are calculated from the formula $\Delta T_1 = T_1 41 \cdot 30 QD$ which is easily derived from Equation I.

(*b*) It should be observed that the values of ϕ given in the preliminary note (*Journ. Washington Acad. Sci.*, 1911, i., 260) were calculated by a formula which holds strictly only so long as ϕ, or the difference between T and θ, is small. The more accurate mode of calculation from Equation III. of the present paper leads to somewhat higher numerical values of ϕ, but does not alter the order of the ϕ values; so that this change does not affect the argument.

The most obvious mechanical property with which to compare the series of ϕ values is the flow pressure (see Note 9). This was determined for a series of metals by Tammann, Verigin, and Levkojeff (*Ann. Phys.*, 1903, x., 649); later, and independently, by Kurnakof and Zhemchuzhny (*Zeit. Anorg. Chem.*, 1909, lxiv., 174). Arranged in the order of decreasing ease of flow, the metals follow in the order K, Na, Pb, Tl, Sn, Bi, Cd, Zn, Sb, a sequence which is identical with that deduced thermodynamically and presented in Table I. But not only is the sequence of ϕ values identical with that of the low pressure; it is practically identical with the sequence obtained when the metals are arranged in the order of *any* of their elastic properties for which measurements have been made. This is shown by Table II., in which have been brought together all the data available on the elastic properties, namely, compressibility, hardness, tensile strength, elastic limit, elastic modulus, and modulus of rigidity.

From Table II. it is evident that, as the value of ϕ increases, the compressibility decreases, and the values of the other elastic properties increase steadily. The exceptions to this statement are very few as regards any one property, and vary irregularly as we pass from one property to another; in other words, there are no systematic divergences between the sequence of the metals as derived from the thermodynamic relationship discussed in this paper and that obtained when they are arranged progressively with reference to any one of their elastic properties. The slight divergences are no greater than one might expect from the uncertain character of the thermal data, on the one hand, and of the elastic constants on the other. Indeed, excellent agreement could have been obtained by selecting for each metal an appropriate value from the somewhat discordant data for the elastic constants in the Landolt-Börnstein-Meyerhoffer Tabellen; but it was deemed more commendable to take a general mean of all the values there given, as it was impracticable to determine just which values represent most accurately the true elastic constants of the various metals.

The purely elastic properties of metals have often been collated and compared, and it has been surmised repeatedly that these properties are some function of the melting-point of the metal (see Note 10). But, so far as the writer is aware, no one has advanced further than a statement of the general parallelism between elastic properties and melting-point—a statement to which there are some notable exceptions, lead, aluminium (see Table II.), also a large number of alloys, which seriously limited its scope and usefulness. When arranged with reference to the function of the melting-point deduced in this paper, the above two metals cease to be exceptions (see Note 11).

One other piece of presumptive evidence in favour of this point of view may also be mentioned, namely, a comparison of the values of ϕ with the flow pressures of tin as determined by E. Jänecke at a series of temperatures (*Metallurgie*, 1911, viii., 68). In default of knowledge of the variation of Q with temperature and pressure, we may justifiably consider Q and D as constants. For any one metal therefore Equation III. may be written, since T_1 is also constant,—

$$\phi = K_1 - K_2 \log \theta \quad \text{(IV.)},$$

where K_1 and K_2 are constants, the values of which depend upon Q, D, and T_1. The graph of Equation IV., which gives the variation of ϕ with θ, is very similar to the curve plottled from Jänecke's results; with increasing temperature both diminish at about the same decreasing rate.

From the above, then, it appears to be true that the mechanical properties of metals are correlated with the amount of pressure—assumed to act on the solid alone—requisite to cause the metal to melt at or near the ordinary temperature. This pressure in turn depends upon the melting-point, the density, and the heat of melting of the metal. The first two of these quantities are known to be periodic functions of the atomic weight, and there is every reason to believe that the heat of melting, and therefore also ϕ, is. Therefore, reasoning from the observed parallelism, we should expect some, or all, of the elastic properties to be periodic functions. So far, thorough measurements have been made only on the compressibility, which, according to Richards, shows marked periodicity.

The remarkable concordance shown in Table II., which can hardly be due to coincidence, suggests that the "flow" of metals—or, indeed, every *permanent* distortion of a crystalline solid—is due to an actual fusion (with subsequent re-solidification) of the crystals. The validity of this view is supported by a large number of well-known facts, *e.g.*, that a metal requires progressively less effort to cause it to weld—or to forge it—the higher its temperature. Moreover, it is corroborated by a large number of observations, which demonstrate the existence of important differences between metal which has "flowed" or has been subjected to deformation of any kind and the same metal in the annealed condition.

All the available evidence (see Note 12) goes to show that there is:—(*a*) A difference in the energy content of the strained and unstrained metal, which is manifested in a difference between the two forms—(1) in their electrolytic potential when immersed in a solution, (2) in their thermo-electric power, (3) in their heat of solution; (*b*) a difference in structure manifested in differences in—(1) microscopic appearance, (2) mechanical properties—hardness, tensile strength, &c., (3) density (see Note 13), (4) conductivity for heat or electricity, &c. For any one metal these differences vanish about a single temperature common to all—thus for silver at about 260°—that is, at the temperature which annealing proceeds with appreciable rapidity.

Notes.

1. *Cf.*, J. H. Poynting, *Phil. Mag.*, 1881, [5], xii., 32; Ostwald's "Lehrbuch der Allgemeinen Chemie," 2 Aufl., vol. ii., II., p. 374; or Roozeboom's "Heterogend Gleichgewichte," vol. i., p. 213.

2. I am much indebted to Prof. Lewis for bringing to my attention this method, which is so much more succinct

TABLE II.—*Relative Values of the Elastic Constants of Metals* (see Note).

Metals in order as in Table I.	Compressibility. (*a*).	Hardness. (*b*).	Tensile strength. (*c*).	(*d*).	Elastic limit. (*e*).	Lower. (*f*).	Upper. (*f*).	Elastic (Young's) modulus. (*g*).	Rigidity modulus. (*h*).	(*i*).
K	31·5	0·5	—	—	—	—	—	—	—	—
Na	15·4	0·4	—	—	—	—	—	—	—	—
Pb	2·2	1·5	2·0	21	0·3	25	102	17	5	0·80
Sn	1 7	1·8	2·1	36	4	34	55	34	16	1·50
Bi	2·8	2·5	—	—	—	—	—	32	12	—
Cd	1·9	2·0	—	48	—	28	109	71	17	2·31
Al	1·3	2·9	—	—	—	283	600	70	29	2·55
Zn	1·5	2·5	13	—	10	125	770	78	31	—
Ag	0·84	2·7	22	272	12	—	—	70	39	2·67
Cu	0·54	3·0	25	316	12	203	2780	108	42	4·37
Pd	0·38	4·8	—	—	27	—	—	103	46	—
Pt	0·21	4·3	29	—	26	—	—	161	52	6·46

NOTE.—It is to be noted that the values given in the table are *relatively* only, and are not always expressed in the same units (*e.g.*, columns *c* and *d*, *e* and *f*, *h* and *i*):—

(*a*) As given by Richards and collaborators (*Journ. Am. Chem. Soc.*, 1909, xxxi., 156).
(*b*) According to Rydberg ("L.-B.-M. Tabellen," p. 57).
(*c*) "L.-B.-M. Tabellen," p. 53.
(*d*) Wertheim (1848) quoted by Faust and Tammann (*Zeit. Phys. Chem.*, 1911, lxxv., 118).
(*e*) "L.-B.-M. Tabellen," p. 53.
(*f*) As determined by Faust and Tammann (*loc. cit.*).
(*g*) and (*h*) General mean of the (sometimes very discordant) values given in "L.-B.-M. Tabellen," p. 43.
(*i*) Horton (*Trans. Roy. Soc.*, A, 1905, cciv.).

than the mode of derivation which I had at first made use of.

3. For a definition and discussion of the term "activity," see Lewis, "Outlines of a New System of Thermodynamic Chemistry, *Proc. Am. Acad.*, 1907, xliii., 259; *Zeit. Phys. Chem.*, 1907, lxi., 129.

4. Lewis, Equations V. and VIII., *Proc. Am. Acad.*, 1907, xliii., 266; *Zeit. Phys. Chem.*, 1908, lxi., 137.

5. This lowering is, of course, relative to the melting-point when that pressure which now acts on the liquid alone (the solid being subject to pressure in excess of this) acts on both solid and liquid. In other terms, if the melting-point is denoted by T with subscripts and superscripts to represent the pressure acting on the solid phase and liquid phase respectively, then $T^{P}_{P+\Delta P}$ is always lower than T^{P}_{P}, the magnitude of this lowering being dependent on the excess of pressure ΔP acting on the solid. Now T^{P}_{P} may be higher or lower than $T_{1}{}^{1}$ (the ordinary melting-point at atmospheric pressure), according as the volume change on melting is positive or negative; consequently, in some cases $T^{P}_{P+\Delta P}$ may be higher than $T_{1}{}^{1}$, but this will be so only when ΔP is small compared to P, a contingency which, we believe, does not affect the main considerations advanced in this paper.

6. Tammann, *Zeit. Anorg. Chem.*, 1904, xl., 54, with K and Na; Johnston and Adams, *Am. Journ. Sci.*, 1911, xxxi., 501; *Zeit. Anorg. Chem.*, 1911, lxxii., 11, with Sn, Bi, Cd, Pb at pressures up to 2000 atm.; Bridgman, *Proc. Am. Acad.*, 1911, xlvii., 347, with Hg up to still higher pressures.

7. In the computations which follow, the value of the density at the ordinary temperature was used. This was done because of the uncertainty in the appropriate correction; moreover, our present knowledge of D at the ordinary temperature is so unsatisfactory that it would be altogether futile to apply any such correction, especially as the accuracy of the present values of Q is so doubtful.

8. Excepting iron, on account of the uncertainty of what "iron" is, and the disparity of the recorded values. The value given for nickel in "Landolt-Börnstein-Meyerhoffer Tabellen" (p. 470) as a heat of fusion (taken from Pionchon, *Ann. Chim. Phys.*, 1887, [6], xi., 106) was found, on reference to the original, to be a heat of *transformation* (occurring somewhere between 230° and 400°); consequently nickel could not be included. Similarly, Pionchon's values for iron given in "L.-B.-M." (p. 470) are heats of *transformation*). Mercury and gallium are omitted, since they are liquid at ordinary temperatures. The value of Q for aluminium is somewhat doubtful; it was calculated from the "total heat" (as given in "L.-B.-M.") by means of the specific heat of aluminium (0·30) as given by Bontschew ("L.-B.-M.," p. 383). No alloys could be included owing to lack of the necessary data; in any case, the formula is applicable only to those alloys which melt completely at a definite temperature.

9. The amount of compression required to cause a material to flow is characteristic of the material under specified conditions; but at constant temperature it varies, as is obvious, with the size of the aperture through which the flow takes place; probably also it depends upon the shape of the aperture and upon other subsidiary factors. Hence determinations of flow pressures are comparable only when they have all been made in the same apparatus and in the same way. This condition is fulfilled by the experimental observations cited, which lead to reliable relative values of the flow pressure for a series of metals.

10. No references are given to this, because the author found it impracticable to examine all of the voluminous literature in order to determine with whom each particular suggestion originated. Some of the points are discussed by Kurnakov and Zhemchuzhny (*Zeit. Anorg. Chem.*, 1908, lx., 1; 1909, lxiv., 149).

11. The Formula III. could not be applied to alloys owing to lack of the necessary data. In any case the formula is applicable presumably only to such alloys as melt completely at a constant and definite temperature.

12. *Cf.* G. T. Beilby (*Phil. Mag.*, 1904, [6], viii., 258—276), who discusses the evidence in detail.

13. Kahlbaum, Roth, and Siedler (*Zeit. Anorg. Chem.*, 1902, xxix., 197); Kahlbaum and Sturm (*Zeit. Anorg. Chem.*, 1905, xlvi., 217); Spring (*Journ. Chim. Phys.*, 1903, i., 593; *Rec. Trav. Chim.*, 1904, xxiii., 1). This subject is fully discussed by Johnston and Adams (*Journ. Am. Chem. Soc.*, 1912, xxxiv., 563).

(To be continued).

Catalytic Action of Kaolin on the Combination of Hydrogen and Oxygen.—Jacques Joannis.—The presence of kaolin induces the combination of H_2 and O_2 at temperatures at which it does not take place in glass, viz., at 230° and above. In the conditions investigated by the author the amount of water formed is proportional to the duration of contact. The activity of the kaolin diminishes as the temperature to which it has previously been heated is raised.—*Comptes Rendus*, clviii., No. 7.

THE SCIENTIFIC WEEK.

(From Our Own Paris Correspondent).

Curious Anomaly of Hydrogen.

It is known that one of the most surprising properties of wood charcoal is that which it possesses of absorbing gases with so much energy when it is cooled to the temperature of liquefied air that, in a single moment, with its help, one can make in an enclosed space that curious vacuum—impermeable even to an electric charge—that is named the Vacuum of Hittorf. Up till now it was thought that this property was joined to the respective aptitude of different gases to liquefaction, so that hydrogen, very refractory to liquefaction, could not be much absorbed. However, M. George Claude having applied this property to the formation of his neon tubes, has seen, to his great satisfaction, that the hydrogen given off by the electrodes is rapidly eliminated, whereas the neon subsists. M. Claude next undertook some direct measures, which have shown him that, effectively, hydrogen is the most curious exception to the rule deduced from the aptitudes to liquefaction, since instead of being less absorbed than neon, it is absorbed something like a hundred times more! So then, in these very especial conditions of temperature which exclude the hypothesis of a chemical action, we discover this curious tendency of hydrogen to become absorbed in the metals cobalt, palladium, and platinum, which constitutes one of the most interesting points of its history, and which must probably be sought for, no more in a chemical action, but doubtlessly far rather in the form or the mass of the atom of hydrogen.

Estimation of Traces of Arsenic.

MM. Moreau and Vinet have been led by their former works on the employment of arsenical products as insecticides for the vine, to take notice of the consequences of this employment from a hygienic point of view, and further to study the estimation of very small quantities of arsenic. Their method of estimation consists in causing the arseniated hydrogen, supplied by the matters to be analysed, to act on a solution of silver nitrate. In suitable conditions, completely precised by authors, there is formed a precipitate of silver that affects the form of a ring, the importance of which, by comparison with rings used as types, permits of the appreciation of the amount of arsenic to be determined. The method is remarkably simple and enables the recognition of one thousandth of a mgrm. of arsenic.

Lakes of Soda.

Quite recently some English engineers, who were constructing the Ongonda railway, discovered the soda lake of Magadi in British East Africa. This bed is absolutely unique of its kind, not only by its extent, but by the very remarkable purity of the soda it contains. M. S. Kestner has just given to the French Société des Ingénieurs Civils some interesting information on this natural curiosity. This African lake seems to contain at least 200 millions of tons of carbonate of soda, almost entirely pure. Already, in Egypt, the lakes of Wadi-Natron were known. These latter contain natural deposits of carbonate of soda, but which is much less pure and more difficult to exploit than that of Lake Magadi. According to M. Kestner it is the residues—accumulated during thousands of years—from the concentration of river or spring water running into these lakes, that form basins with no issue, which have been the cause of these deposits. The waters, entirely evaporated, have left behind them, in the lakes of Wadi-Natron and Magadi, all the salts they contained, and generally the carbonate of soda is accompanied by sulphate and chloride. Exceptionally, in the Lake Magadi, only the carbonate of soda is present. M. Kestner thinks, also, that other known beds may be put into exploitation before long, and that it is very likely that other large deposits of this salt may be discovered, probably in more accessible regions and at a cheaper cost than in equatorial Africa. In these conditions is it not possible that the soda industry may eventually disappear in the face of this competition of the natural product?

CHEMICAL SOCIETY.

Ordinary Meeting, March 19, 1914.

Prof. W. H. Perkin, LL.D., F.R.S., President, in the Chair.

Reference was made to the loss sustained by the Society through the death of Daniel Bain (Gateshead), Harry Burrows (Southgate), Robert Kennedy Duncan (Pittsburg), Leonard Clifford Green (Brisbane), Christopher Clarke Hutchinson (Kensington), Joseph William Thomas (Shortlands), and Francis Vacher (Birkenhead).

Messrs. A. P. L. Blaxter and A. Bicknell were formally admitted Fellows of the Chemical Society.

The President announced that Prof. Arrhenius has accepted the invitation of the Council to deliver the Faraday Lecture this year. The lecture, entitled "Electrolytic Dissociation," will be delivered in the Theatre of the Royal Institution (by the courtesy of the Managers) on Monday, May 25, at 6 p.m., and further particulars will be announced later.

Certificates were read for the first time in favour of Messrs. Charles Frank Armstrong, Marhourah Sugar Works, Marhourah, B. and N.W. Railway, Saram, Behar, India; Frederick Stanley Baxter, 119, Albert Street, Regent's Park, N.W.; Robert Odell Bishop, 1, Augustine Road, West Kensington, W.; Hugh Miller Galt, B.Sc., M.B., Elm Croft, Withdean, Brighton; Trevor Edward Hodges, 43, Stapleton Hall Road, Stroud Green, N.; William Whalley Myddleton, M.Sc., 6, Fairfield Road, Latchford Without, Warrington.

A Certificate has been authorised by the Council for presentation to ballot under By-law I. (3) in favour of Mr. Birendranath Maitra, 10, Kalighat Road, Bhowanipur, Calcutta, India.

Of the following papers, those marked * were read:—

*77. "*The Ignition of some Gaseous Mixtures by the Electric Discharge.*" By Hubert Frank Coward, Charles Cooper, and Julius Jacobs.

The pressure of an explosive gaseous mixture may be reduced until ignition becomes impossible with the particular igniting arrangement in use. Such limiting pressures vary considerably with the strength of the igniting electric discharge (see Coward, Cooper, and Warburton, *Trans.*, 1912, ci., 2278, on the ignition of electrolytic gas), but comparable results for various mixtures are obtainable by preserving a constant igniting arrangement of induction coil, cells, spark-gap, &c. The ignition of an explosive mixture the composition of which does not approach too near to the dilution-limit of inflammability proves to be determined chiefly by (1) the energy effect of the discharge itself, a function of the composition and pressure of the mixture; (2) the thermal conductivity of the mixture; and probably (3) an activation of the oxygen. The ignition of such a mixture is therefore a question of strength of spark, and maintained concentration of its energy until the end of the pre-flame period, rather than of the thermal effect of combustion in the path of the spark. Once a true flame is initiated in a homogeneous explosive mixture, its propagation is assured, except in very narrow vessels.

These considerations serve to explain some curious experimental results, of which the following may be quoted:—A series of hydrogen-oxygen mixtures showed a radidly falling ignition-pressure with increase in oxygen-content until with 60 to 85 per cent of oxygen the ignition-pressure became almost constant. In one apparatus, electrolytic gas at 80 mm. pressure could be inflamed after

the addition of (a) 23 mm. of electrolytic gas itself, or (b) 8 mm. of oxygen or more up to at least 720 mm., or (c) 90 mm. of hydrogen or more up to 210 mm.

Similarly, electrolytic gas much below its ignition-pressure has been ignited after the addition of suitable amounts of nitrogen, carbon dioxide, and even argon.

The cyanogen—oxygen, methane—oxygen, and ethylene—oxygen series of mixtures have been examined; also the carbon-monoxide—oxygen series, alone and with various diluents. The carbon monoxide experiments provided the chief evidence respecting the activation of oxygen in the discharge.

*78. "*Hydrazoximes of Methyl- and Phenyl-glyoxals.*" By BIMAN BIHARI DEY.

The hydrazoximes of methylglyoxal, phenylglyoxal, and *iso*nitrosomethylglyoxal, and their benzylidene, benzoyl, and acetyl derivatives, as well as their corresponding azines, have been prepared. The semicarbazones and phenylcarbamylhydrazones of *iso*nitroso-acetone, -acetophenone, &c., were also described.

*79. "*The Action of Chromic Chloride on the Grignard Reagent.*" By GEORGE MACDONALD BENNETT and EUSTACE EBENEZER TURNER.

It has been shown that when anhydrous chromic chloride is brought into contact with an ethereal solution of magnesium phenyl bromide, chromous chloride and diphenyl are produced in the quantities required by the equation—

$$2CrCl_3 + 2C_6H_5{\cdot}MgBr = 2CrCl_2 + C_6H_5{\cdot}C_6H_5 + MgBr_2 + MgCl_2.$$

No organo-metallic derivatives of chromium could be isolated.

Besides diphenyl, very satisfactory yields of dibenzyl, 4 : 4'-dimethyldiphenyl, and *aa'*-dinaphthyl have been obtained by similar reactions. A reaction of the same kind was obtained using magnesium *iso*amyl iodide, but the yield of di-*iso*amyl was much less satisfactory.

*80. "*The Influence of Solvents on Molecular Weights. Part I. Salts.*" By WILLIAM ERNEST STEPHEN TURNER and CORNELIUS THEODORE POLLARD.

Before any valid interpretation can be drawn of the results of molecular-weight measurements in solution, it is essential that the influence of the medium should be understood. This influence may be physical or chemical, and it is obvious that if the effect of the solvent can be expressed by some physical rule, the interpretation of results is much simplified.

From an examination of existing data, the view had been expressed (Turner, *Trans.*, 1911, xcix., 880) that the main factor influencing the value of the molecular weights of salts in solution is the dielectric character of the solvent, and in order to test how far this view was valid, a systematic review of the subject was undertaken, experiments being made for the purpose on chlorides, bromides, iodides, and a nitrate of organic ammonium bases, dissolved in fourteen solvents. To the new data obtained were added those previously obtained by one of the authors (Turner, *loc. cit.*, and *Trans.*, 1912, ci., 1923), and by other workers, bringing up the total to twenty-three solvents. The following conclusions were drawn:—

1. The molecular weight of an electrolyte is, in a general way, a function of the dielectric character of the solvent, and the statement (Turner, *loc. cit.*) that electrolytic dissociation and molecular association are complementary phenomena, the former appearing in solvents of high, the latter in those of low, dielectric constant, is amply confirmed.

p-Toluidine, of low dielectric constant, is exceptional, but the low results found in this solvent with most of the substances dissolved may be due to combination. Nitrobenzene, in which certain organic substances are strongly associated, falls into line as a solvent for iodides and nitrates, producing apparent dissociation in accordance with its high dielectric constant.

2. Whilst no sharp line can be drawn, association of a salt occurs, in moderately dilute solutions, when the dielectric constant of the solvent falls below 18, but the extent of association depends both on the solvent and the solute.

3. For solvents of low dielectric constant, the degree of association is not strictly parallel to the dielectric constant.

4. As a general rule, the degree of association of similarly constituted salts falls in the order iodide > bromide > chloride, both in associating and dissociating solvents, thereby affording further evidence of the complementary character of association and dissociation.

Chlorides, in some cases, behave exceptionally.

5. Rise of temperature has a marked influence in decreasing the degree of association of salts.

6. The common view that associated substances dissolved in associated solvents become thereby dissociated is disproved in the case of salts. Such simplification only occurs when the associated solvent possesses a high dielectric constant.

81. "*Deliquescence. Part I. The Deliquescence of Salts of Ammonium Bases.*" By CYRIL JAMES PEDDLE.

Little or no previous systematic study of deliquescence appears to have been made, descriptions of the deliquescence of substances being either the result of visual tests or of exposing a known weight of material on a watch-glass or other vessel. Both methods are crude, and have been proved by experience to be deceptive.

The chief factors influencing deliquescence are the temperature and humidity of the atmosphere, the area and depth of the substance used, and the size of the particles of the exposed material. In order to obtain accurate values all these factors must be allowed for, especial care being taken to ensure the air being constantly saturated with moisture.

The amount of water absorbed by 1 grm. of substance is termed the deliquescence of that substance, and results have been obtained accordingly. In addition, the number of grm.-molecules of water absorbed by 1 grm.-molecule of salt was calculated, this value being termed the molecular deliquescence. Some evidence of the rate of absorption was obtained from the ratio—

$$\frac{\text{Molecular deliquescence}}{\text{Time of exposure.}}$$

Amongst homologous compounds, additive properties are absent, the phenomenon of deliquescence appearing to be only constitutive. Solubility is also related to deliquescence, although the relation is a complicated one, being most marked in the case of chlorides.

In general, the order of deliquescence in a series falls with increase in molecular weight, and in the case of corresponding haloid salts the chloride is most deliquescent and the iodide least. The introduction of aromatic radicles brings about a large decrease in deliquescence, whilst salts containing only aromatic radicles are non-deliquescent.

Many of the salts examined had a deliquescence comparable with that of common inorganic drying agents.

82. "*Some Derivatives of as-Dipropyl- and Diamyl-oxamic Acids.*" By HARFORD MONTGOMERY ATKINSON.

Dipropylamine and diamylamine easily react with ethyl oxalate, forming the esters of dipropyl- and diamyl-oxamic acids. The following derivatives were described:—

Ethyl dipropyloxamate, $CO_2Et{\cdot}CO{\cdot}N(C_3H_7)_2$, b. p. 143°/10 mm., which, by the action of ammonia, gives as-*dipropyloxamide*, $NH_2{\cdot}CO{\cdot}CO{\cdot}N(C_3H_7)_2$, m. p. 96—97°.

as-*Dipropyloxamonitrile*, $CN{\cdot}CO{\cdot}N(C_3H_7)_2$, b. p. 120°/14 mm., which, when treated with hydrogen sulphide, yields as-*dipropylthiooxamide*, $NH_2{\cdot}CS{\cdot}CO{\cdot}N(C_3H_7)_2$, m. p. 129—130°.

Thiopiperidylglyoxylamide, $NH_2{\cdot}CS{\cdot}CO{\cdot}NC_5H_{10}$, crystals, m. p. 66—67°; *thio-as-diethyloxamide*, $NH_2{\cdot}CS{\cdot}CO{\cdot}NEt_2$, m. p. 126—127°; *thio-as-dimethyloxamide*, m. p. 120—121°.

Dipropyloxamic acid, $CO_2H{\cdot}CO{\cdot}N(C_3H_7)_2$, m. p. 73—74°, and its *chloride*, $COCl{\cdot}CO{\cdot}N(C_3H_7)_2$, b. p. 112—116°/14 mm., which, with dipropylamine, gives *tetrapropyl*-

oxamide, $[CO{\cdot}N(C_3H_7)_2]_2$, m. p. 38—39°, and by the action of heat furnishes *dipropylcarbamyl chloride*, $COCl{\cdot}N(C_3H_7)_2$, b. p. 118—120°/21 mm.; *piperidine-1-carboxyldipropylamide*, $C_5H_{10}N{\cdot}CO{\cdot}N(C_3H_7)_2$, b. p. 173°/10 mm.; *dipropyldiamylcarbamide*,—

$$N(C_3H_7)_2{\cdot}CO{\cdot}N(C_5H_{11})_2,$$

b. p. 185°/12 mm.; *dipropylformamide*, $HCO{\cdot}N(C_3H_7)_2$, b. p. 102°/17 mm.; *ethyl diamyloxamate*, $CO_2Et{\cdot}CO{\cdot}N(C_5H_{11})_2$, b. p. 166—167°/10 mm.; as *diamyloxamide*, $NH_2{\cdot}CO{\cdot}CO{\cdot}N(C_5H_{11})_2$, m. p. 182°; *diamylformamide*, $HCO{\cdot}N(C_5H_{11})_2$, b. p. 141—145°/18 mm.; *diamylcarbamyl chloride*, $COCl{\cdot}N(C_5H_{11})_2$, b. p. 147—149°/14 mm.; and *phenyldiamylcarbamide*, $C_6H_5{\cdot}NH{\cdot}CO{\cdot}N(C_5H_{11})_2$, m. p. 204°.

(To be continued).

INSTITUTE OF CHEMISTRY.

Mr. William Macnab delivered his second lecture on "*Explosives*" at King's College, on Thursday, March 26, 1914.

After referring to the restrictions and regulations imposed on the industry by the Home Office in the interests of safety, the lecturer gave a description of the manufacture of explosives, more particularly nitro-cellulose and nitro-glycerine. Thomson's Displacement process for making gun-cotton is the most important improvement which has been made in this branch, and it has the great merit of producing better gun-cotton at less cost than the old processes, and at the same time of being much less unpleasant and dangerous to the workpeople.

Nathan and Rintoul's Nitrator-Separator for making nitro-glycerine was illustrated and described. Here again progress was in the direction of simplicity and safety, one of the features being the abolition of all cocks in the pipes through which the nitro-glycerine has to pass. The charge of glycerine which can be nitrated in one operation has now increased to 1400 lbs.

The uniformity and excellence with which the manufacture of cordite can be carried out is shown in the small margin in velocities and pressures allowed by the Government.

In the new 15-in. gun the charge of cordite is about 420 lbs., and with a muzzle velocity of 2500 ft. seconds, the variation allowed is only $\pm$ 15 ft. seconds.

Referring to the ammonium nitrate class of explosives which consist chiefly of two or three non-explosive ingredients mixed together, the lecturer considered it a distinct hardship and contrary to the public interest that such explosives should be penalised by having to be manufactured under the same expensive conditions as their much more dangerous rivals. They should be allowed to compete on the market with the advantage of their inherent properties.

The test for "permitted" explosives was gone into, its object being to prevent explosions of gas or dust in coal mines from the use of explosives.

The filling charge for shells most generally used in the principal countries is now trinitrotoluol, which is a safe and powerful explosive. Tetranitroaniline is the strongest solid explosive body and is also very stable, and would appear to offer many advantages for torpedoes, military blasting work, and possibly as a charge for shells and aeroplane bombs.

A more pleasing use for explosives has arisen in connection with agriculture. America and the colonies have been the chief fields for this development, but the planting of trees and rejuvenating of existing orchards by means of explosives would appear to be worthy of careful study and trial in this country.

The effect of exploding a cartridge judiciously placed in the ground is to shake it up and fissure it to a far greater extent than can possibly be done by spade work, and new trees planted in such prepared ground make much more rapid and vigorous growth and bear better, while in an old orchard the ground can be similarly opened and shaken without injury to the standing trees, which, having less dense soil to penetrate with the roots, make corresponding good growth and get a new lease of life. Finally, it was pointed out that chemistry is the foundation of the explosive industry, and that the chemist should play the leading technical rôle in it. A high standard of conduct and conscientious carrying out of work are necessary, seeing that carelessness or a mistake may endanger or sacrifice the lives of many people.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clviii., No. 7, February 16, 1914.

Researches on Acid Salts of Dibasic Acids. *d*-Metallic Camphorates.—E. Jungfleisch and Ph. Landrieu.—The authors have prepared the camphorates of sodium, lithium, ammonium, barium, strontium, calcium, magnesium, manganese, cobalt, piperidine. The investigation of these compounds shows that the neutral or dimetallic camphorates are very stable in presence of water, which does not dissociate them. The acid camphorates are unstable towards water, and are all split up into free acid and neutral dimetallic salt. This indicates that the acid camphorates are the result of the union of camphoric acid with the dimetallic salt; *i.e.*, that they are compounds analogous to the acid salts of monobasic acids.

Constitution of Gaseous and Liquid Chlorides of Cyanogen.—V. Grignard and G. Bellet.—When organo-magnesium compounds act on the halogen derivatives of cyanogen two different reactions may occur:—(i.). Cyanogen iodide gives only the iodine derivative of the organic radical. (ii.). Gaseous cyanogen chloride, on the contrary, gives, with fatty or aromatic magnesium compounds, very little of the chlorine derivative but chiefly the nitrile. With the bromide of cyclo-hexyl magnesium, however, it behaves in exactly the opposite way, giving chlorocyclohexane and very little nitrile. Apparently the gaseous chloride in the free state has the carbylamine structure, but is tautomerised by organo-magnesium compounds, the fatty and aromatic compounds effecting the transformation very rapidly and completely. The liquid chloride is probably the chloroformic nitrile.

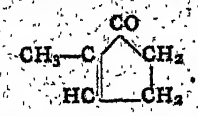
Some Double Chromates.—M. Barre.—Two double chromates of calcium and potassium exist. Both are easily decomposed by water. The chromate formed below 45° has the formula $CrO_4K_2.CrO_4Ca.2H_2O$. If this is kept at 60° in presence of a solution of CrO_4K_2 the second salt, $CrO_4Ca.CrO_4K_2$, is formed. Strontium chromate gives only one double salt, viz., $CrO_4Sr.CrO_4K_2$, and barium chromate behaves similarly. Lead chromate also gives $CrO_4Pb.K_2CrO_4$. This salt is decomposed by water, but its decomposability diminishes as the temperature rises.

Heat of Formation of Manganese Sulphide.—S. Wologdine and B. Penkiewitsch.—The authors have determined the heat of formation of manganese sulphide by observing the heat disengaged by the direct union of finely powdered Mn and S. The numbers obtained are always higher than that of J. Thomsen, who gave −44·390 cal. for the hydrated sulphide. From the authors' experiments the heat of formation of the sulphide from metallic manganese and octahedral sulphur is probably 62·901 cal. per molecule.

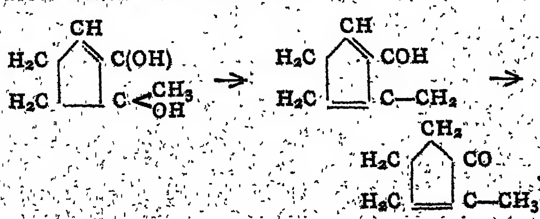
Preparation of Metaphosphate of Molybdenum Sesquioxide.—A. Colani.—Metaphosphate of molybdenum sesquioxide, $3P_2O_5.Mo_2O_3$, can be prepared by reducing molybdic acid dissolved in metaphosphoric acid by hydrogen at a dull red heat, or by heating anhydrous MoS_2 with orthophosphoric acid in a current of carbon dioxide. The same phosphate may be obtained by reducing at a red heat in a current of CO_2 molybdic acid dissolved in metaphosphoric acid by an excess of molybdenum sulphide. Red phosphorus can also be employed as reducing agent. Molybdenum metaphosphate is stable in dry air; when heated it is oxidised only superficially. In a sealed tube in absence of air it is attacked by water at 250—300°, phosphoric acid being liberated and a small quantity of hydrogen. It is soluble in a sealed tube at 200° in sulphuric solutions of potassium bichromate or iodic acid. It is not attacked by HCl, HNO_3, or H_2SO_4 at 100°, but H_2SO_4 acts upon it at its boiling-point, SO_2 being given off.

Syntheses by means of Mixed Organometallic Derivatives of Zinc. 1.4-Acyclic Diketones.—E. E. Blaise.—Of the 1.4-acyclic diketones only one is known, viz., acetonyl acetone. Others can be prepared by first getting the succinic ether of an acid alcohol, and then the acid dichloride, which is condensed with the organo-zinc compound. Finally, the biscyclo-acetal formed is subjected to alcoholysis by means of methyl alcohol containing a little hydrochloric acid. In general oxyisobutyric acid gives the best results, and a good yield of symmetrical dipropionyl ethane can be obtained from it.

Synthesis of Methylcyclopentenone. — Marcel Godchot.—In 1894 Looft isolated from wood-tar an unsaturated cyclic ketone to which he ascribed the formula—



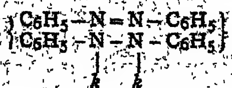
The author has now confirmed this formula by the following synthesis:—Starting from 1.2-cyclopentane dione by Grignard's reaction he obtained the glycol 1-methyl-2-cyclopentene-1,2-diol. When this glycol is heated to 100° for three hours in presence of oxalic acid and water it is dehydrated and the ketone obtained is identical with the above ketone. The reaction is—



Berichte der Deutschen Chemischen Gesellschaft.
Vol. xlvii., No. 3, 1914.

Nitrogen Luminescence.—A. Koenig and E. Elöd.—It has been shown that luminescence in nitrogen after the passage of electric discharges appears equally strongly, even after purification of the gas from traces of oxygen, provided that the gas is free from metallic vapour. If the latter is present the luminescence is very much weakened or altogether prevented. If oxygen, as well as metal, is present the luminescence is increased, the metal being oxidised. An excess of oxygen, however, diminishes the luminescence. All these phenomena are compatible with the assumption that the nitrogen is made active.

Addition of Metals to Multiple Bonds.—W. Schlenk, J. Appenrodt, A. Michael, and A. Thal.—It has already been shown that the carbonyl group, containing the carbon oxygen double bond, possesses the power of forming addition products with the alkali metals, and the authors have now found that in suitable experimental conditions other double bonds can be saturated by the alkali metals. The alkali metal is best used in the form of powder, and it is essential that the action should take place in absence of air and moisture. The best solvent to use is ether, and the action may be allowed to take place at room temperature. The rates at which the reactions occur differ very much; in some cases the action begins as soon as the substances are brought into contact, while in others they have to be shaken together for days. Metallic addition products of substances containing the following groups have been prepared: $-{>}C=C-$ (*e.g.*, disodium stilbene, $C_6H_5.CHNa.CHNa.C_6H_5$); ${>}C=N-$ (*e.g.*, disodium anilino - diphenyl - methane, $(C_6H_5)_2CNa.NNa.C_6H_5$); $-N=N-$ (*e.g.*,—

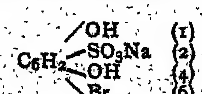


${>}C=O$ (*e.g.*, disodium benzhydrol, $(C_6H_5)_2C{<}^{ONa}_{Na}$).

Remarks on G. Steimmig's Article "Synthetic Rubber from Isoprene."—C. Harries.—According to Steimmig (*Ber.*, 1914, xlvii., 350; CHEMICAL NEWS, 1914, cix., 156) no artificial rubber has been prepared from isoprene which exactly resembles natural rubber, the product being always a mixture of 1.5- and 1.6 dimethylcyclooctadiene-1.5. The author, however, states that he can prove that the artificial rubber which he obtained in the autumn of 1909 from the Elberfelder Farbenfabriken, does not possess the composition described by Steimmig, but is a fairly pure polymeric 1.5-dimethylcyclooctadiene.

Bulletin de la Société Chimique de France.
Vol. xv.-xvi., No. 3, 1914.

Monobromsulphonic Hydroquinones and their Transformation into Monobromosulphoquinones.—A. Seyewetz and J. Paris.—A sulphonic bromohydroquinone can be prepared by sulphonating the bromohydroquinone obtained by the action of bromine in solution in chloroform upon hydroquinone dissolved in a mixture of ether and chloroform. The aqueous solution of this sulphonic bromohydroquinone immediately reduces silver nitrate in the cold. It can be transformed into bromosulphonic quinone by oxidising with sodium bichromate and sulphuric acid at about 20°. Bromosulphonic quinone is a strong oxidising agent and immediately liberates iodine from an acid potassium iodide solution in the cold. When concentrated hydrobromic acid acts on sulphonic quinone below 20°—



is obtained. Above 20° 2 . 6-dibromohydroquinone is obtained.

No. 4, 1914.

Absorption of Ultra-violet Rays by Coloured Organic and Mineral Solutions.—MM. Massol and Faucon.—The twenty-one dyes investigated by the authors can be classed in two categories:—(i.) Those which absorb only radiations of short wave-length and exhibit unilateral absorption. These include Paris violet, erythrosine, eosine, acid fuchsine, &c. (ii.) Those which exhibit bilateral absorption, *e.g*, malachite green, auramine, &c. The substances which best cut off the invisible ultra-violet rays are the yellow chrysoine, naphthol yellow, yellow potassium chromate, potassium ferrocyanide; and the reds, bordeaux B, solid red, crystallised ponceau, scarlet R.

Preparation of Cyanuric Acid from Urea and Chlorine.—A. Béhal.—The best method of preparing cyanuric acid from urea and chlorine is as follows:—600 grms. of commercial urea are heated to 110°, and dry chlorine (obtained from 320 grms. of potassium permanganate and 1600 cc. of hydrochloric acid) is led in. The temperature is then raised to about 150°, and, after the mass has become practically solid, to 180°. Finally a solid mass weighing 700 grms. is obtained. This is powdered and heated till alkaline gas is no longer evolved (loss of weight = about 100 grms.). The mass is then extracted with boiling water, and ammonia and ammoniacal copper sulphate are added. The precipitate formed is washed and decomposed with nitric acid. The raw crystallised cyanuric acid obtained is fractionally recrystallised. The first product of the reaction is chlorourea, which probably reacts with the urea to give biuret. From the biuret and urea a triuret may be formed, and this liberates ammonia and gives the cyclic product cyanuric acid.

Synthesis with Isobutyrone. — MM. Murat and Amouroux.—Isobutyrone condenses like butyrone with different types of organomagnesium compounds to give the tertiary alcohols and their derivatives foretold theoretically. The yields are generally lower in this new series. The alcohols obtained are heavier than those prepared from butyrone, and the index of refraction is a little higher. The phenylurethanes of these alcohols cannot be obtained owing to the ease with which they are dehydrated, but they are well defined by their physical constants and by their decomposition products.

Action of Anhydrides and Acid Chlorides on Tertiary Benzylamines.—M. Tiffeneau and K. Fuhrer.—The anhydrides and acid chlorides are capable of breaking the bond between the atoms of nitrogen and carbon in various tertiary amines. Thus by heating *p*-methoxybenzyldimethylamine with acetic anhydride to the boiling-point of the latter the following decomposition occurs:—

$$OCH_3.C_6H_4.CH_2.N(CH_3)_2 \xrightarrow{CH_3COOCOCH_3} OCH_3.C_6H_4.CH_2(OCOCH_3) + CH_3.CO.N(CH_3)_2.$$

The corresponding primary and secondary amines do not undergo the similar reaction, but simply give amides. Only the compounds of the structure $Ar.CH_2.NRR'$ can have their nitrogen-carbon bond broken thus. Apparently chlorides and anhydrides only induce the rupture of the nitrogen-carbon bond in tertiary benzylamines because they are relatively feeble reagents, and it is only when the benzyl group is substituted that the decomposition can be brought about by simply heating to the boiling-point of the reagent. With unsubstituted benzylamines the reaction is always incomplete, and it is necessary to heat for a long time in a sealed tube.

Iodohydrines and Alkyliodohydrines Derived from Cyclohexylpropene.—B. de Rességuier.—Hypoiodous acid and its ethers can be fixed at ethylene double bonds in two ways. The author has studied its action upon a mixed cyclic aliphatic hydrocarbon cyclohexylpropene, and has obtained two different compounds, from which cyclohexyl-1-propanal-3 and cyclohexyl-1-propanone-2 can be prepared, $C_6H_{11}CH_2CHOH{-}CH_2I \xrightarrow{-HI} C_6H_{11}CH_2COCH_3$ and $C_6H_{11}CH_2CHI{-}CH_2OH \xrightarrow{-HI} C_6H_{11}CH_2CH_2CHO$.

Barium Chloride Method of Determining Free Alkali in Soda and Soap.—André Kling, Victor Genin, and D. Florentin.—The barium chloride method of determining free alkali in soda, as described in the text-books, is incapable of giving accurate results if such salts as sodium silicate or sodium borate are present. It is quite accurate, however, if the precipitation is effected in alcoholic solution. The same method can be used for the analysis of soaps containing borates or silicates; there is, however, no object in employing it if the soaps contain only fatty ether and especially oleates, the solubility of barium oleate in alcohol being appreciable.

MISCELLANEOUS.

The Chemical Laboratory Fresenius at Wiesbaden.—During the Winter Term 1913-14, the Chemical Laboratory Fresenius was attended by 29 students (including 7 ladies). Of these 21 were from Germany, 3 from Luxemburg, 2 from Russia, 1 from England, 1 from Switzerland, and 1 from Brazil. There were two assistants in the Instruction Laboratory, and twenty-nine in the private Laboratories (Versuchsstationen). To the teaching staff of the Institution belong the Directors, Geh. Regierungsrat Prof. Dr. H. Fresenius, Prof. Dr. W. Fresenius, and also Dr. R. Fresenius and Dr. L. Grunhut. The next Summer Term begins on April 24. Ladies are admitted as students. During the Winter Term 1913-14, besides the scientific work, a great number of analyses were undertaken in the different departments of the Laboratory (Versuchsstationen) on behalf of trade, manufacture, mining, agriculture, hygiene, justice, and government.

Royal Institution.—The following are the lecture arrangements at the Royal Institution, after Easter:—Dr. Walter Wahl, two lectures on "Problems of Physical Chemistry—(1) Study of Matter at High Pressures; (2) Structure of Matter at Low Temperatures" (experimentally illustrated). Prof. W. Bateson, Fullerian Professor of Physiology, Royal Institution, two lectures on—(1) "Double Flowers," (2) "The Present State of Evolutionary Theory." Prof. D'Arcy W. Thompson, two lectures on Natural History in the Classics—(1) The Natural History of the Poets Homer, Virgil, and Aristophanes; (2) The Natural History of Aristotle and of Pliny." Prof. A. Fowler, two lectures on "Celestial Spectroscopy—Experimental Investigations in connection with the Spectra of the Sun, Stars, and Comets." Three Literary Lectures. Prof. Svante Arrhenius, three lectures on "Identity of Laws in General and Biological Chemistry." Prof. Silvanus P. Thompson, two lectures on "Faraday and the Foundations of Electrical Engineering." Dr. T. E. Stanton, two lectures on "Similarity of Motion in Fluids—(1) The Theory of Similarity of Motion in Fluids and the Experimental Proof of its Existence; (2) The General Law of Surface Friction in Fluid Motion." Prof. C. J. Patten, two lectures on "Bird Migration." Prof. J. W. Gregory, two lectures on—(1) "Fiords and their Origin," (2) "Fiords and Earth Movements." Mr. Sigismund Goetze, two lectures on "Studies on Expression in Art—(1) Origin and Development, (2) Right Expression in Modern Conditions." The Friday Evening Meetings will be resumed on April 24, when the Astronomer Royal, Mr. F. W. Dyson, will deliver a Discourse on "The Stars around the North Pole." Succeeding Discourses will probably be given by Mr. E. F. Benson, Prof. Karl Pearson, Prof. F. Keeble, Mr. Robert Mond, Prof. J. C. Bose, Prof. W. H. Bragg, and other gentlemen.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Mercury Fulminate.—I should be obliged for information as to bodies formed when fulminate of mercury is dissolved in a solution of sodium thiosulphate. The equation is also requested, as I have looked in numerous text-books in vain.—F. O.

MEETINGS FOR THE WEEK.

Monday, 6th.—Royal Institution, 5. General Meeting.
—— Society of Chemical Industry, 8. "By-Products from Peat," by F. Mollwo Perkin. "Sulphuric Acid—the Swing of the Pendulum," by H. E. Armstrong. "Table of Specific Gravities of Spirits for Use with Bedford's Tables," by J. N. Rakshit and S. N. Sinha. "Viscosity of Rubber Solution," by R. Gaunt.

THE CHEMICAL NEWS.

Vol. CIX., No. 2837.

ATOMIC WEIGHTS.

By F. H. LORING.

The study of radio-active phenomena affords strong evidence that many of the stable elements are complex, in that they comprise atoms differing in atomic weight from each other which are non-separable by chemical means. Prof. Soddy gave expression to this idea (Chem. News, cviii. 168).

The discovery of a companion gas to neon of different atomic weight, yet spectroscopically indistinguishable, and the supposition that certain radio-elements, although differing materially in atomic weight, are indistinguishable by this test (supported by one definite experiment), is in harmony with the belief that the atom is conditioned by the electron rather than by its atomic mass. The mass may, as it were, be the vehicle for retaining the electron or electrons. As a radio-element loses β-particles (negative electrons), its chemical properties become altered without an appreciable alteration in its mass. It is true that the loss of an α-particle (= helium atom carrying two positive charges of electricity) coincides with a change in properties, but probably there is a rearrangement of the electrons in the atom in this case. As the loss of two positive charges alters the chemical character of the atom, it might be inferred that the loss of two negative charges would restore the atom to its original chemical state. A stepping-back of the element in the Periodic Table, in consequence of the loss of a β-particle, has been observed (see citation above).

If, therefore, the electric system within the atom is a real differentiating factor, then it seems probable that the fractional atomic weight values in themselves are of no material moment, and one might conceive the elementary atomic weights as whole numbers. Moreover, these numbers, to be in harmony with the radio-elements, should differ by four units, being built up of helium atoms. The possibility of H_3 as a nucleus in the odd-number series (see below) suggests itself.

This idea would reconcile the Prout theory that all the elements are fixed or stable polymerides of hydrogen as a fundamental unit, hydrogen being taken, however, as absolute unity. Then helium itself may be four atoms of hydrogen combined in such a way as to be extremely stable. The existence of X_3 discovered by Sir J. J. Thomson, which is now believed to be a polymeride of hydrogen, supports this conjecture, since this tri-atomic molecule is fairly stable. H_4, therefore, might be even *more* stable, and thus become the helium atom.

I have shown in the Chemical News, cix., 143, that copper, silver, and gold probably are made up of associate elements (atoms) differing in atomic weight, non-separable by chemical means, and exactly whole numbers. This idea in a general way was suggested by Sir William Crookes (see Chem. News, 1887, lv., 95).

In this connection it may be of interest to note that P. de Heen (*Bull. Acad. Roy. Belg.*, 1913, pp. 680—694) gave an experimental demonstration of the variability of the molecule and atom. The facts brought to light seem to show that the silver-chloride molecule can be modified by suitable treatment, and that the different forms of silver salt are to be regarded as derived from silver atoms which are not identical. In other words, the experiments seem to afford evidence of transformation of normal silver into its meta elements. Whether this experiment is to be interpreted in this particular way need not be discussed here, suffice it to say that the idea of *meta* elements is one that is no doubt engaging the attention of many scientists. The meta elements of Crookes correspond with the isotopes of Soddy.

It will be seen that probably the chemical elements can be broadly classified thus:—

I. Whole-number atomic-weight elements which have no associates differing from them in atomic weight.

II. Whole-number atomic-weight elements composed of, or containing, chemically non-separable associates of different atomic weight.

If the foregoing argument be sound in principle, then the atomic-weight values, as determined experimentally by chemical methods, should be verifiable, and the values for the associate members ascertainable. The associates or isotopes may be designated thus:—Cu^{I}, Cu^{II}, Ag^{I}, Ag^{II}, &c. The true atomic weights may be correspondingly expressed thus:—$Cu^{I}63$, $Cu^{II}67$, &c. Furthermore, the relative numbers of respective atoms may be shown thus:—$Cu^{I}63_7$, $Cu^{II}67_1$, $Ag^{I}107_7$, $Ag^{II}111_2$, &c.

Group VII. is very interesting, as it contains, in my opinion, branches (see "Studies in Valency," pp. 23 and 25), and I have attempted to ascertain the various values for this curious group. A word of caution is, however, necessary. The method employed renders it difficult to fix upon the proportionate numbers, and doubt arises as to whether one is justified in confining the selection of whole numbers to the Rydberg Atomic Series. When this series fails to supply a proper figure, other whole numbers may be taken. This procedure may be objected to, but it is not safe to be influenced too strongly by the radio-active precedent. Square brackets will be introduced to designate those values which are not taken from the Rydberg series.

The following tentative values have been worked out by this method:—

Chlorine	=	$(40\times1+35\times10)/11$	=	$35{\cdot}45\dot{4}\dot{5}$
Manganese	=	$([54]\times1+55\times10)/11$	=	$54{\cdot}90$
Iron	=	$(55\times1+56\times10)/11$	=	$55{\cdot}90$
Nickel	=	$(55\times1+59\times10)/11$	=	$58{\cdot}63$
Cobalt	=	$59{\cdot}00$		
Ruthenium	=	$(99\times1+[102]\times10)/11$	=	$101{\cdot}72$
Rhodium	=	$(100\times1+103\times10)/11$	=	$102{\cdot}72$
Palladium	=	$(104\times1+107\times10)/11$	=	$106{\cdot}72$

Commenting on the above atomic-weight values it will be observed that they agree with the experimental ones, and in some cases the same atomic weight is common to two or three elements. This peculiarity would be considered as fatal to the scheme, if it were not for parallel cases amongst the radio-elements, suggesting that though the atomic weights are the same, the electronic or electric systems differ in the atoms, and indeed they would not therefore be isotopic.

Referring to the radio-group, it will be seen that perhaps Hönigschmid's value for radium, 225·97, is near to a possible true value 226, but a question arises as to whether the disintegration is quite as simple as supposed, considering that associate atoms may in some way alternately disintegrate, as suggested by the branching in the different series.

The radio-active gases, and the inactive gases which are not radio-active, should give, by the positive ray method, double lines if these elements be mixtures unless some unsuspected condition arises. The lines might be so close as to appear as one line if the atomic weights of large magnitude differ by only one unit. Ten argon atoms of atomic weight, 40 each to every 1 of atomic weight 39, would give a mean value of 39·909. Similarly, krypton would be 82·909. But in the latter case a non-Rydberg value, 82, would be introduced. It seems probable that the positive-ray experiments will throw some light upon the question of meta elements.

I may add in conclusion that, using the constants 10 and 1, the following mean values are obtainable:—Mg = 24·27; Si = 28·27; Br = 79·909; Ba = 137·36. With the constants 1 and 7, Al = 27·125. Constants 3 and 7 are possible ones for some of the rare earth metals.

It seems significant to observe that aluminium and magnesium are the first elements in the odd and even series which have well-authenticated fractional differences of appreciable magnitude, implying in the case of aluminium that possibly it is made up of six helium atoms condensed round a H_3-nucleus (=27), and in association with a helium polymeride without such a nucleus (=28) in proportion 7:1. The preceding elements therefore may be fundamental types (I.), whilst the succeeding ones are for the most part more complex (II.). Assuming a continuation of the atomic disintegration process, it should then stop at these elements.

March 22, 1914.

SOME NOTES ON THE ESTIMATION OF PHOSPHORUS IN IRON AND STEEL.

By HARCOURT PHILLIPS, F.C.S.

Of the various schemes from time to time proposed for estimating phosphorus in steel, the chief are those based on initial separation of the element as phospho-molybdate salt, from a solution containing free nitric acid and ammonium nitrate. The details of the process are set forth in the text-books dealing with the requirements of a steel works laboratory.

The general experience of analysts has confirmed the observation that to ensure entire separation of the phosphorus in a minimum of time, the volume of solution should be neither too large nor the nitric acid in too great excess. Violent agitation and the presence of a fair amount of ammonium nitrate much assist speedy precipitation. Fresenius gives 40° C. as a suitable temperature, and, after vigorous stirring of the solution, sets it aside for twelve hours; a plan of working probably designed to lessen the chance of co-precipitating molybdic trioxide and at the same time ensure complete separation of all phosphorus.

My own experience I expect will be that of other analysts, viz., that a sufficiency of molybdate reagent assisted by vigorous agitation will separate all phosphorus after twenty minutes.

Precipitation of phosphoric acid from iron and other metals by molybdenum was a plan worked out by Sonnenschein (*Journ. Prakt. Chem.*, liii., 342), and has been practised for over fifty years, though the constitution of the yellow precipitate was, until recently, imperfectly known. In recent years F. Hundeshagen (*Zeit. Anal. Chem.*, xxviii., 141) has carefully examined the precipitate to learn its composition, and the conditions in which the pure phospho-molybdate is formed. Hundeshagen (*loc. cit.*) describes the precipitate, and assigns the formula $(NH_4)_3PO_4.12MoO_3$, a salt with a phosphorus content of 1·65 per cent when dried at 130° C. or thereabouts.

Brearley and Ibbotson ("Analysis of Steel Works Materials," p. 344) give an abstract of Hundeshagen's paper.

The yellow precipitate, once obtained and washed free from acid and other matter, can be dealt with in one of several ways. A common practice is to collect it on a previously weighed or counterpoised filter-paper, to wash with dilute nitric acid, then alcohol, and to dry in water-oven, and re-weigh. The phosphorus content is found by the factor 0·0165. This process is usually called the "direct method," to distinguish it from those wherein the washed precipitate is either dissolved in ammonia, and treated as by Brearley and Ibbotson's lead molybdate plan, or, again, is dissolved in soda as in J. O. Handy's scheme (Chemical News, lxxvi., 324). A further indirect plan is that described in Blair's "Chemical Analysis of Iron" (1908, p. 93), in which the phospho-molybdate is reduced by Zn and H_2SO_4, and the solution titrated with permanganate. Other indirect methods are based on the initial separation of the phosphorus by means of stannic oxide, ferric oxide, &c., with conversion of the resultant phosphate into ammonium magnesium phosphate, and final weighing as $Mg_2P_2O_7$.

Schemes such as these are far too slow for a busy works analyst. In the course of my practice I have employed the "direct method" for some years, and presume that other analysts will have observed, as I have, the appearance of a greyish blue stain on the dried filter-paper. The stain appears above the precipitate, sometimes on the outside, and often at the apex of the filter. The stain suggests slight reduction of the MoO_3 by the cellulose. Should the stain be well developed the paper will be friable and break easily at the apex.

I may say that the stain seldom appears unless there be a remnant of nitric acid in precipitate or paper, or unless the filter and precipitate have lain too long in the water-oven. Should the stay in the oven have been unduly prolonged some stain will always appear, though the paper and precipitate shall have been copiously washed with cold water to ensure complete removal of acid.

The gradual loss of weight which a filter and precipitate sustain by prolonged drying is shown by the following examples:—

The phospho-molybdate from 2 grms. of separate steels was collected and thoroughly washed on previously dried and weighed 7 cm. filters. The final wash was with alcohol.

	A.	B.
Weight of precipitate after quarter of an hour in oven	0·0361	0·031
Weight of precipitate after one hour in oven, stain slight	0·0349	—
Weight of precipitate after three hours in oven, stain more developed	0·0324	0·028

Taking 0·0361 grm. in Sample A to be correct, the phosphorus will be 0·0297 per cent.

This steel, by Ibbotson's lead molybdate method, gave 0·030 per cent, and by the magnesia plan on 4 grms. of the metal 0·0307 per cent phosphorus.

It would appear, then, that after the final wash with alcohol the filter should not stay in the water-oven longer than fifteen to twenty minutes.

It was the appearance of the stain which led me to try an alternative plan of dealing with the precipitate, a plan I will now describe.

The following solutions were prepared:—

Di-sodic phosphate.

Nitro-molybdate.

Nitric acid, 1·2 sp. gr.

A 2 per cent nitric acid wash.

A sodium silicate solution, of which 5 cc. contained SiO_2 = 3 mgrms. Si.

A mean of four estimations of the phosphorus in 50 cc. of the sodic phosphate by the magnesia plan gave 0·00798 grm. The solution was measured in all cases from a burette divided into one-tenth cc. and fitted with a float.

The nitro-molybdate was prepared according to the formula given by Brearley and Ibbotson on p. 56 of their book. When made as they direct the solution will remain quite free of deposit for many weeks. The sodium silicate was acidified with nitric acid immediately before use, and was a quite clear solution.

The procedure was this:—After measuring off 50 cc. of the phosphate into a stoppered flask there were added 30 cc. of the $1·2HNO_3$, 10 cc. of ammonia (0·880 diluted with an equal volume of water), and then 30 cc. of the molybdate. After vigorous shaking and warming to 40° C. the flask was set aside for an hour before filtration of the liquid, though the upper layer had cleared in fifteen minutes. The precipitate, collected on a 9 cm. filter of close texture, was freed of all salts by aid of the 2 per cent nitric acid wash. This done, *all acid* was then removed by washing with cold water. (The filtrate will usually be quite clear, provided the paper has the requisite texture and has been snugly adjusted, when wet, to the side of the

funnel). On completion of the washing the funnel was placed over a 6½ cm. light weighed dish, and the precipitate dissolved from the filter by ammonia.

What precipitate remained in the flask was collected in the same manner and added to the contents of the dish, which need not exceed 30 cc. if the washing has been done with small affusions at a time of hot water. The contents of the dish, after being taken to dryness on the steam-bath, were further heated in the water-oven until the residue had a constant weight.

Whatever the exact composition of the saline residue may be, it will contain the phosphorus of the 50 cc. of standard phosphate, viz., 0·00798 grm., so that, given concordant weights of residue, the operator can deduce a factor therefrom.

A first experiment gave me 0·534 grm. of residue, hence $\frac{0 \cdot 00798}{0 \cdot 534}$ gives the factor 0·01494. An average of six experiments gave 0·0151, of which the highest was 0·0152 and the lowest 0·0148.

For the experiments to follow, chiefly made with measured portions of the standard phosphate, I calculated the phosphorus content by the factor 0·0151. I should state that the ammoniacal solution of the phospho-molybdate was in all cases re-filtered through the same filter before evaporating, when iron was present. The precaution is necessary, since some little iron is co-precipitated with the phospho-molybdate, and clings to it or to the paper in spite of the washing with the 2 per cent nitric acid.

Na_2HPO_4 solution. Cc.	Phosphorus taken. Grm.	Weight of residue dried at 100° C.	Phosphorus per cent assumed, taking 2 grms. of a steel.	Phosphorus per cent found by experiment.
20	0·003192	0·2120	0·1596	0·1600
10	0·001596	0·1074	0·0798	0·0810
10	0·001596	0·1080	0·0798	0·0815
5	0·000798	0·0532	0·0399	0·0401
5	0·000798	0·0525	0·0399	0·0396
2·5	0·000399	0·0270	0·0199	0·0203
2·5	0·000399	0·0275	0·0199	0·0207
2·5	0·000399	0·0281	0·0199	0·0212
2·5	0·000399	0·0268	0·0199	0·0202
2·5	0·000399	0·0269	0·0199	0·0203

The annexed estimations of phosphorus were made in the presence of as much ferric nitrate as would be equal to 2 grms. of iron. In the first four experiments soluble silicic acid equal to 3 mgrms. of Si were added. This would represent 0·15 per cent of Si in a steel, and the precipitated phospho-molybdate was collected after one hour's standing. In the second four experiments *a*, *b*, *c*, and *d*, soluble SiO_2 equal to 12 mgrms. of Si was added, and the precipitate allowed to stand for twelve hours before filtering. After weighing the saline residues I dissolved them in ammonia, and set the solution aside until next day. A slight flocculent deposit was then observable, in which I confirmed the presence of silica and iron. I am not inclined, however, to attribute the higher percentage of phosphorus in *a*, *b*, *c*, and *d* entirely to the above, since the error may be partly ascribed to co-precipitated molybdic trioxide—an effect of the twelve hours repose.

Na_2HPO_4 solution. Cc.	Phosphorus taken. Grm.	Weight of residue dried at 100° C.	Phosphorus per cent assumed taking 2 grms. of a steel.	Phosphorus per cent found by experiment.
10	0·001596	0·1090	0·0798	0·0822
5	0·000798	0·0533	0·0399	0·0402
5	0·000798	0·0540	0·0399	0·0407
5	0·000798	0·0566	0·0399	0·0427
5	0·000798	0·0634	0·0399	*a.* 0·0478
5	0·000798	0·0584	0·0399	*b.* 0·0440
5	0·000798	0·0624	0·0399	*c.* 0·0471
5	0·000798	0·0605	0·0399	*d.* 0·0456

In conclusion, I will give the estimation of phosphorus in a chromium steel. The test was made by four methods. For the magnesia method 5 grms. of steel were taken.

	Phosphorus, per cent.
Direct plan	0·0178
Ibbotson's plan	0·0180
J. O. Handy's plan ..	0·0177
Magnesia plan	0·0182
H. Phillips's plan	0·0181

As regards speed, the quickest is perhaps Handy's plan. When making use of it I find it convenient to balance the acid and alkali cc. to cc., and to check occasionally the strength of the soda by means of freshly precipitated and washed phospho-molybdate, which is readily prepared by aid of a standard di-sodic phosphate, of which 50 cc. represent 8 mgrms. of phosphorus.

Court Chambers,
Bolton, Lancashire.

AN EXPERIMENT ON THE COLOURS OF SOME COBALT SALTS IN SOLUTION.

By J. E. MARSH.

A SOLUTION of sodium chloride and cobalt chloride in a mixture of water and acetone, which is pink when cold, separates on warming into two solutions, the upper one being light blue in colour and the lower dark blue. The upper layer is expelled gradually, and the lower layer changes its colour gradually as the temperature is raised. The solutions will mix again on cooling to the original homogeneous pink solution. When cooled without mixing the upper layer fades to an almost colourless solution, which becomes blue again on warming, while the lower layer changes in colour from blue to pink. The concentration of the solution may be varied within certain limits. A good effect is given by taking the following proportions by weight:—1 Sodium chloride; 2 hydrated cobalt chloride, $CoCl_2 . 6H_2O$; 7·7 acetone; and 8·7 water. This solution contains the salts in the proportion of $2NaCl$ to $CoCl_2$, and about equal volumes of acetone and water. The solution separates on heating into nearly equal volumes, and the colours are not too dark. The solution should be contained in a sealed glass tube and heated by placing in hot water. Cobalt chloride alone without the sodium chloride will bring about the separation in much the same way, but a higher temperature is required.

Potassium and cobalt bromides in acetone and water give much the same effect. With lithium and cobalt chlorides the solution when cold is blue. On warming, the light and dark blue layers are obtained, and on cooling without mixing the upper layer retains its colour, while the lower layer changes from blue to pink. The following proportions by weight give a good colour effect:—1 Lithium chloride; 2·8 hydrated cobalt chloride; 9·7 acetone; 10·5 water.

AN ENCLOSED CADMIUM ARC FOR USE WITH THE POLARIMETER.*

By T. MARTIN LOWRY and H. H. ABRAM.

IT is no longer necessary at the present time to emphasise the importance of rotatory dispersion, *i.e.*, of measuring rotatory powers for a whole range of wave-lengths, instead of recording only one point on an unknown curve. But as regards methods of measurement, the necessity of using pure monochromatic light may still be urged. Light filters must be regarded as suited only for a first approximation, since the optical mass centre of the transmitted light may vary with the source of light, and in any case it is impossible to get exact readings of big

* Contribution to a General Discussion on "Optical Rotatory Power," held before the Faraday Society, March 27, 1914.

rotations, which no longer give an extinction. Spectral purification of white light is better, but the "monochromatic illuminator" requires careful use to be sure that the wave-length used is actually that recorded on the drum of the instrument.

In the early days of the measurement of rotatory dispersion it was necessary to use a large range of wave-lengths, as the form of the curves was quite unknown. Thus, in 1908, measurements of the rotatory power of methyl camphorcarboxylate were given for 26 wave-lengths, namely:—

Li, 6708. Na, 5893. Tl, 5351.
Hg, 5790, 5769, 5461, 4359.
Cd, 6438, 5086, 4800, 4678.
Ag, 5469, 5209. Zn, 6364, 4811, 4722, 4680.
Cu, 5782, 5700, 5219, 5154, 5105, 4705, 4651, 4587, 4378.

Twenty-four wave-lengths were used in measuring the rotatory power of quartz in the visible region of the spectrum, and readings (as yet unpublished) have been taken by a photographic method for over 700 wave-lengths in the visible and ultra-violet regions of the spectrum.

In the case of substances whose rotatory dispersion is anomalous, it is still desirable to extend the observations to include a large number of wave-lengths, extending over a wide range of the spectrum. But in the case of substances whose rotatory dispersion is normal a much smaller range of wave-lengths will suffice; in fact, in the case of all those substances whose rotatory power can be expressed by the simple formula—

$$\alpha = \frac{k}{\lambda^2 - \lambda_0^2}$$

only two observations are required in order to determine the two constants of the equation. These two fundamental observations are most conveniently made with the green and violet rays of the mercury spectrum, since the ratio $\alpha_{4359}/\alpha_{5461}$ is something like 10 times more sensitive than, *e.g.*, the ratio $\alpha_{5461}/\alpha_{5893}$. The simple apparatus required for measuring this ratio is being exhibited by the courtesy of Messrs. A. Hilger, who have supplied the polarimetric equipment, and the Westinghouse Cowper-Hewitt Co., who have supplied the mercury-lamp.

It still remains, however, to establish a satisfactory method of proving that the curve of rotatory dispersion is strictly normal. This can be done to a rough approximation by reading one or two additional wave-lengths and then plotting $1/\alpha$ against λ^2, when the whole of the readings should fall upon a straight line. The most convenient readings to take for this purpose are Na 5893 and Li 6708. But the sodium-line is too near the mercury-green to reveal any but the grossest anomalies, and the lithium line, which represents the "furthest south" in the direction of the infra-red, cannot be relied on to give readings of the same order of accuracy as in the case of the two mercury lines. The simple formula given above was therefore verified in the first place only when the readings for 23 substances of similar dispersive power were averaged in order to eliminate individual errors of observation. It was at this point that the enclosed cadmium arc made its appearance, with the result that it promises to effect a revolution in polarimetric methods comparable with that which resulted from the introduction of the mercury arc.

The methods by which the cadmium spectrum was first rendered available for polarimetric work in the visible region were shown before the Physical Society in June, 1909, and were described in a paper which was published in the *Proc. Phys. Soc.*, vol. xxii., and also in the *Phil. Mag.* of August, 1909. The apparatus consisted of two electrodes of a silver-cadmium alloy, rotating in opposite directions on spindles driven from a small electromotor. On striking an arc between the electrodes a brilliant spectrum was emitted which included the lines of silver and of cadmium. Apart from the annoyance caused by the flickering of the arc this apparatus can be used very effectively if the polarimeter is provided with a constant-deviation spectroscope to purify the light before it enters the polariser. But it cannot well be used with the simpler apparatus, in which the light is resolved only by a direct-vision prism on the eye-piece, as the unextinguished parts of the spectrum are usually too dazzling to permit of easy reading on any one line at the extinction-position. The "method of producing an intense cadmium spectrum" by means of a silver-cadmium arc was therefore "not put forward as the ideal way of producing an intense cadmium spectrum, but rather as an intermediate stage in the development of the perfect cadmium lamp of the future." The search for the perfect cadmium lamp has been in progress ever since, and by the generous co-operation of Mr. F. Stanley, of Messrs. A. Hilger & Co., we are able to exhibit—not perhaps the perfect lamp itself, but one of its more or less distant ancestors in the process of its evolution.

In the lamp the arc is run between water-cooled electrodes of *solid* cadmium; this is important, partly because it checks the vaporisation of the metal, but mainly because if the metal is allowed to melt it is liable to crack the tube whenever the lamp is started or stopped. The lamp must be used in conjunction with a Gaede pump, as the metal gives off considerable quantities of gas under the influence of the electric discharge, and these must be pumped off in order to maintain the vacuum. Occasionally, when the vacuum is good, the arc will start itself by merely switching on the current, but usually it is necessary to start the arc by a spark; this can be done conveniently by connecting the electrodes to the inner walls of two Leyden jars and connecting the outer walls to the secondary terminals of an induction coil. The light emerges through two windows of quartz. In our most recent lamp we have tried to protect these windows from condensed metal by water-jacketing the ends of the tube to which they are attached, but the water-jacketing must not extend to the central part of the tube, which must remain hot in order to prevent the formation of a conducting bridge of condensed metal. An arch of silica has been provided to bring the arc to the centre of the tube.

The lamp will burn quite well under a pressure of 100 volts, but it has a longer life if the voltage is higher, owing to the fact that an arc of greater length can be kept alight. The extinction of the lamp on the lower voltages is caused most frequently by the distillation of mercury from the electrodes, which thus become shortened unduly. We have tried to check this defect by enlarging the diameter of the tubes containing the metal, but have not yet had enough experience to say how far we have been successful in our endeavours.

The cadmium lamp, which is still in the experimental stage and obviously far from perfect, is only just being brought into actual use in our polarimetric work. We can, however, quote one example of the kind of service it may be expected to render. It was desired to find out in the case of α- and β-methyl-glucoxides, not merely the magnitude of the constants in the dispersion-equation, but also whether these two compounds, containing no less than 5 asymmetric carbon atoms, nevertheless obey rigidly the simple dispersion law. Solutions of the two glucoxides were made, containing 25 grms. in 100 cc., and these were examined in 600 mm. polarimeter tubes. The readings were as follows:—

		α-Methylglucoxide.		β-Methyglucoxide.	
Mercury	Violet..	155·32°	Ratio	33·32°	Ratio
	Green..	94·17	1·649	19·95	1·666
Cadmium	Green..	109·90	Ratio	23·51	Ratio
	Red ..	66·10	1·663	14·09	1·669

It will be seen that the ratios for the two cadmium lines are almost equal to the ratios for the two mercury

lines. Each pair of lines can be read without disturbing the setting of the apparatus, and the cadmium readings (unlike those for lithium) are quite as reliable as the mercury readings and equally suited for working out the "rotation constant" k, and the "dispersion constant" λ_0^2, for either substance. The values of the constants are:—

	k.	λ_0^2.
a-Methylglucoxide—		
From mercury readings ..	25·87°	0·0234
From cadmium readings ..	25·85°	0·0235
β-Methylglucoxide—		
From mercury readings ..	5·40°	0·0274
From cadmium readings ..	5·48°	0·0257

The figures for the *a*-methylglucoxide are remarkable. The "rotation constant" k (which is numerically equal to the "absolute rotation," a_0, *i.e.*, the rotation which would be observed at wave-length $\lambda = \sqrt{1+\lambda_0^2}$) is represented by two values which differ from the mean by only $\pm 0·01°$, an error of 1 part in 2000. The "dispersion-constant," which shows a difference of one unit in the third significant figure, is really (in spite of appearances) still more accurate. Three units in this decimal correspond with a difference of one unit in the fourth figure of the dispersion ratios; the two values given for λ_0^2 correspond therefore with a difference from the mean of 1 part in 10,000 in the actual readings. There can therefore be no doubt whatever as to the validity of the simple dispersion formula to represent the experimental data for this complex substance.

The figures for the *β*-methylglucoxide are less concordant, in part because the readings are five times smaller; but they agree sufficiently well to show that there is no large deviation from the simple dispersion law.

It will be seen from the illustrations given above that the development of the enclosed cadmium arc promises to inaugurate a new era in the measurement of *normal rotary dispersion*. With the help of the new apparatus it will be possible to determine the two fundamental constants of any optically active compound by two methods of equal exactness. Further, the agreement of the two pairs of figures will serve as a check, not merely on the accuracy of the readings (in itself a very important advantage), but also on the strict validity of the dispersion formula in the case of each individual substance.

It is a pleasure, in conclusion, to acknowledge the valuable help that has been received in connection with this work from the Dixon Fund of the University of London.

DETERMINATION OF WATER OF CRYSTALLISATION IN SULPHATES.

By S. B. KUZIRIAN.

CERTAIN substances, *e.g.*, chlorides of barium and calcium, sulphates of sodium, potassium, barium, &c., are completely dehydrated at moderately high temperatures, leaving a definite and weighable compound. Under such conditions, when the substances do not lose anything but water, at a definite temperature, the determination of water of crystallisation can be made with great ease.

Certain other substances, like the minerals talc, topaz, chondrodite, staurolite, do not lose all of the water of crystallisation by simple ignition at moderate temperatures. The high heat of the blast-lamp is in such cases applied for the complete removal of water. This latter step often gives rise to complications when the material to be blasted changes weight otherwise than by loss of water, *e.g.*, by loss of carbon dioxide, fluorine, chlorine, or by accession of oxygen, as when a ferrous compound is ignited in air.

Some other crystalline substances like sulphates and alums of aluminium and chromium are decomposed with loss of material other than water, at temperatures obtainable with an ordinary good-sized Bunsen burner, thus preventing a correct determination of their crystalline water.

Various modifications in treatment have been suggested to avoid complication in water determinations. For instance, in the case of minerals, talc, topaz, &c., fusion with pure and dry sodium carbonate will expel the water which may be absorbed in sulphuric acid and weighed (Hillebrand, *Bull.* 422, United States Geol. Survey, p. 79).

Fusion of such silicates, very finely pulverised, with anhydrous powdered borax, is another method suggested by Jannasch ("Praktischer Leitfaden der Gewichtsanalyse," Leipzig, 1897, 2nd ed.), for the same object. If the silicates are found to contain fluorine, then a retaining layer of granular lead chromate or a previously fused and powdered lead oxide is used in the ignition tube. This process is found objectionable by W. H. Hillebrand for the reason that silicates on fine grinding lose some water (*Bull.* 422 United States Geol. Survey, p. 83).

Magnesia is another substance mentioned in connection with determination of crystalline water in decomposable compounds like silico-fluorides (F. Stolba, *Zeit. Anal. Chem.*, vii., 23). Under definite conditions this flux seems to give satisfactory results, a correction being necessary when the separated metallic oxide, *e.g.*, ferrous oxide, takes up atmospheric oxygen. In the case of decomposable sulphates, however, no attempt has been made to determine their water of crystallisation, while retaining all of the acidic oxide.

In the investigation of the action of sodium paratungstate upon some salts containing a volatile acid radical, both in presence and absence of superheated steam, described in previous papers (*Am. Journ. Sci.*, [4], xxxi., 497; xxxvi., 301, 305), it has been shown that this acidic salt is able to expel the acidic oxides of carbonates, nitrates, chlorides, chlorates, &c., completely and with great ease. But sulphates which are stable on simple ignition, for example, the sulphates of sodium, potassium, barium, and even calcium and manganese, do not lose appreciably their sulphur trioxide either in absence or in presence of superheated steam on fusion with the paratungstate. For example, 0·2 grm. of sodium sulphate on fusion with the paratungstate did not lose in weight at all. The same amount of manganous sulphate when fused with the same flux lost only 0·0010 grm. of sulphur trioxide. Calcium sulphate on similar treatment lost only 0·0002 grm., and further heating did not occasion further loss. The explanation is that the basic sodium oxide of the sodium paratungstate combines with volatile sulphur trioxide of the sulphates to form the non-volatile sodium sulphate. The presence of a considerable excess of the acidic tungsten trioxide apparently does not influence the reaction.

The following may serve as a typical representation of the reaction:—

$$5\overset{\text{II}}{M}SO_4+5Na_2O.12WO_3=5Na_2SO_4+5\overset{\text{II}}{M}O.12WO_3.$$

Since sodium paratungstate does not expel the volatile sulphur trioxide from sulphates, it should be capable of serving a useful purpose as a flux in the expulsion of the water of crystallisation of sulphates ordinarily decomposable by heat; and any sodium tungstate containing less of this acidic oxide should be similarly serviceable. In the preliminary investigation of this application of the sodium tungstates a nearly neutral sodium tungstate was prepared, and a portion of the dry material was weighed and placed in a platinum crucible, a weighed portion of a decomposable sulphate—viz., crystalline copper sulphate ($CuSO_4.5H_2O$)—was mixed well with the tungstate, and the covered crucible heated with a very low flame of a Bunsen burner waving under it. (In order to purify the commercial material, which ordinarily contains sodium carbonate, it was fused in a large platinum dish over the blast, and pure tungstic trioxide was added until carbon

dioxide ceased to bubble out). After driving off most of the water, the crucible was heated to low redness and the mixture fused, cooled, and weighed. The loss apparently corresponded exactly to the theoretical loss of water in $CuSO_4.5H_2O$. The fusion was repeated several times and weighed over again, but no further loss in weight was found. So it appears that while crystalline copper sulphate loses some of its sulphur trioxide when heated by itself at the temperature which is necessary for its complete dehydration, no loss of the acidic oxide occurs in presence of sufficient amount of neutral sodium tungstate when the mixture is heated over a Bunsen flame to dull red heat. It is possible to keep the mixture in quiet fusion for fifteen to twenty minutes without losing any sulphur trioxide. Sodium tungstate thus serves excellently to retain the sulphur trioxide at a temperature sufficiently high to dehydrate the sulphate completely.

To determine the water of crystallisation in sulphates by weighing the water evolved, as well as by loss on ignition, the following procedure was tried. A hard glass ignition tube, about 15 inches long and 1¼ inch in diameter, was placed upon a small furnace; each end was fitted with a perforated (one hole) rubber stopper soaked in hot paraffin for a moment and wiped carefully; and one end of it was connected with a large air-drying apparatus, while the other end was joined to a sulphuric acid weighing tube. The sulphuric acid tube was connected to a calcium chloride drying tube to prevent the entrance of any moisture into the weighing tube *from* outside, and the calcium chloride tube was connected to an aspirator. The ignition tube was thoroughly dried by heating it for at least forty-five minutes, and passing a rapid current of dry air with the aid of the aspirator. The efficiency of the apparatus was evident from the fact that when, after such drying, the sulphuric acid weighing tube was connected with the ignition tube and a blank test made, by running the apparatus for one hour, a gain of only 0·0003 grm. in the weight of the weighing tube resulted, for which a correction was applied in the subsequent work. After having the apparatus thus in readiness, exactly half a grm. of the sulphate was mixed well with 3 grms. of sodium tungstate in a porcelain boat, ignited and weighed previously. The boat and its contents, weighed together, were introduced into the ignition tube. The ignition was started at first very gently by passing a current of hot dry air over the boat, at a rate of 3 bubbles a second, for a period of fifteen minutes. The temperature was carefully and gradually increased until the mixture went into clear fusion. By waving a Bunsen flame around the ignition tube and short delivery tubes the condensed moisture was volatilised. After the apparent disappearance of all moisture the remaining traces of it were forced into the sulphuric acid weighing tubes by a more rapid current of dry air, while continuing the heating of the ignition and delivery tubes for at least twenty minutes. After this period the heating was stopped, while a rapid current of dry air was passed for about ten minutes. The weighing tube was disconnected, stoppered with the glass plugs used as stoppers in the first weighing, brought as nearly as possible to the original temperature (by setting it aside for a few moments), wiped around with a filter-paper, and weighed. The gain in weight of the weighing tube was recorded. After disconnecting the weighing tube from the ignition tube, the delivery tube leading into the ignition tube was plugged carefully to avoid any moisture. The boat was taken out while rather hot, cooled in a desiccator over sulphuric acid, and weighed, and the loss in weight was recorded. It was found that if the procedure was carried out with the utmost care, observing all the precautions, the loss in weight of the porcelain boat, within experimental error, corresponded to the gain in weight of the sulphuric acid tube, and this corresponded closely to the theory for water in the crystallised sulphates. Repeated fusions of the contents of the boat did not occasion any further loss in weight, thus proving that under the conditions there is no loss of sulphur trioxide.

The sulphuric acid weighing tube used was a side-neck U-tube filled with glass beads, and the ends of the large tube were sealed. The rubber connecters were air-tight so that the weighing tubes would not gain in weight over night. It is desirable that the sulphuric acid in the drying apparatus and in the weighing tube should have the same absorbing power; for this reason the sulphuric acid in the weighing tube was changed after every four determinations.

The determination of the water of crystallisation in copper sulphate and in other sulphates was carried out under the conditions cited above, with special precaution to avoid loss by decrepitation of the salt while yielding its water. After mixing the sulphate well with sodium tungstate, another portion of the flux was put upon the surface of the mixture to form a trap, and thus avoid mechanical loss, and the mixture was heated with utmost care for a long time at a temperature not exceeding 70° C. Following are some of the results obtained with various sulphates:—

TABLE I.—*Determination of Water of Crystallisation in Various Sulphates.*

Sulphate taken.	Dried sodium tungstate taken.	Loss of the porcelain boat after ignition.	Gain of sulphuric acid weighing tube.	Difference.
Grm.	Grm.	Grm.	Grm.	
Copper Sulphate.				
$CuSO_4.5H_2O$.				
0·2000	4	0·0707	0·0701	−0·0006
0·2000	4	0·0715	0·0712	−0·0003
Aluminium Sulphate, $Al_2(SO_4)_3.18H_2O$.				
$Al_2(SO_4)_3.18H_2O$.				
0·2000	4	0·0897	0·0913	+0·0016
0·2000	4	0·0900	0·0894	−0·0006
0·2000	4	0·0907	0·0915	+0·0008
0·2000	4	0·0925	0·0935	+0·0010
Nickel Sulphate, $NiSO_4.6H_2O$.				
$NiSO_4.6H_2O$.				
0·2000	3	0·0822	0·0831	+0·0009
0·2000	3	0·0832	0·0833	+0·0001
0·2000	3	0·0826	0·0825	+0·0001
Chrome Alum, $[K_2SO_4.Cr_2(SO_4)_3].24H_2O$.				
$K_2SO_4Cr_2(SO_4)_3.24H_2O$.				
0·2000	4	0·0807	0·0800	−0·0007
0·2000	4	0·0755	0·0755	0·0000
0·2000	4	0·0780	0·0794	+0·0014
Potassium Alum, $[K_2SO_4.Al_2(SO_4)_3].24H_2O$.				
0·2000	3	0·0915	0·0923	+0·0008
0·2000	3	0·0911	0·0929	+0·0018
0·2000	3	0·0910	0·0915	+0·0015
0·2000	3	0·0915	0·0928	+0·0013

From the results detailed in the above table it is evident that there is no loss other than water during the fusion. Even from aluminium and chromium sulphates which lose their acidic oxide on simple ignition, no sulphur trioxide is volatilised in the presence of sodium tungstate. The water of crystallisation of these sulphates may, therefore, be determined in a remarkably short time and with great accuracy with the use of this flux, and the advantage to be derived is obvious and needs no particular comment.

In the case of an acidic sulphate the entire amount of the acidic oxide will be retained by the tungstate, and the water of constitution as well as the water of crystallisation will be evolved.

The extension of the use of this flux to the estimation of water in salts other than sulphates is, for lack of time, left to some future date.—*American Journal of Science*, xxxvi., p. 401.

A CORRELATION OF THE ELASTIC BEHAVIOUR OF METALS WITH CERTAIN OF THEIR PHYSICAL CONSTANTS.*

By JOHN JOHNSTON.

(Concluded from p. 163).

According to Beilby (*loc. cit.*), the process of deformation is always accompanied by a partial transformation of the metal to an "amorphous" form (see Note 14), which acts as a cementing material for the untransformed grains. According to Faust and Tammann (*Zeit. Phys. Chem.*, 1911, lxxv., 108), on the other hand, the change of properties on deformation is parallel to the production of smaller crystallites. Whichever be the correct interpretation—if, indeed, these views are mutually exclusive (see *prox.*)—the fact remains that deformation of a metal is accompanied by changes in its properties. These changes are such that they would be rather difficult to account for reasonably, except on the very simple supposition that an actual melting has occurred.

Against this view it might be urged that the pressures required to cause the metals to melt about the ordinary temperature are so great that they are unlikely to occur in practice. But this objection loses weight when it is remembered that the brunt of any strain, to which a crystalline mass is subjected, is borne by a small number of crystals at any one time. When these crystals give way, others take up the strain, and so on. In this way, relatively very small total forces could produce very considerable pressures locally, pressures sufficient to cause melting at those points. This process would be like the method of tearing a pack of cards, which consists in holding them in such a way that the force comes on only one card at a time.

This point of view accounts plausibly for other aspects of the behaviour of metals—for instance, the "hardening" of metals and the increase of strength following upon deformation; but before proceeding to discuss this, it seems advisable to outline a mechanical picture of the probable mode of action of unequal pressure upon a metal.

Poynting (*Phil. Mag.*, 1881, [5], xii., 32), and also Le Chatelier (*Zeit. Phys. Chem.*, 1892, ix., 338) have used this conception of unequal pressure to account for regelation—the consolidation of a mass of loose snow at 0° into a block of solid ice. The pressure, due to the superincumbent material, lowers the melting-point at the surface of contact of adjacent grains by an amount Δt. The water formed flows out into the interstices of the snow grains, where it is at a pressure of 1 atmosphere but at a temperature of $-\Delta t$, and is in contact with ice at 0°; consequently it freezes again. This process continues until all the interstices are filled up; that is, until a solid block of ice is formed.

Considerations analogous in every respect are applicable to systems of solid grains in contact with water or an aqueous solution. In such cases pressure acting only on the solid increases its solubility, and renders the solutions supersaturated as soon as they are out of contact with the *compressed* solid. Le Chatelier accounts in this way for the consolidation of natural beds of rock-salt, gypsum, calcium carbonate, &c., and he showed by direct experiment that consolidation could be produced in this way.

The behaviour of metals under the action of a differential compression we conceive to be identical with that pictured above for ice. Namely, that metal melts wherever the pressure reaches the appropriate value, flows into the interstices where the pressure is smaller, and solidifies again, with the formation in general of very small crystals, by reason of the exceedingly rapid rate of re-crystallisation.

The effects of unequal pressure are analogous to those produced by a shearing stress; or, perhaps, one should say rather that the effects of a shearing stress are those produced by what we have termed unequal pressure. Now a longitudinal tensile stress can always be resolved into a uniform dilatation and a shearing stress, just as a longitudinal compressive stress can be regarded as composed of a uniform compression and a shearing stress. Hence the conception of unequal pressure, and its effect on the melting-point of a crystalline substance, is equally applicable to all permanent deformations, whether produced by compression or by tension.

When pictured in the way outlined in the above paragraphs, it is obvious that one might expect a parallelism between the ϕ values and certain of the mechanical properties; in all cases, namely, in which the property in question—for instance, tensile strength or flow pressure—implies in any way a permanent deformation of the material, the latter being presumed always to be a manifestation of a real melting produced wherever the stress reaches the appropriate value. In regard to the purely elastic properties—those, *e.g.*, compressibility, which imply no *permanent* change in the material—the parallelism can hardly be ascribed to a melting; but it may very well be an expression of the fact that the elastic properties and the ϕ values as calculated in this paper are all functions of some one determining factor. (This question is treated later). But even if this is so, it in no wise detracts from the plausibility of the view that deformation is conditioned by an actual melting; for there is no apparent necessary connection between the modes of action of stresses which produce deformation and of those which do not.

The possibility of accounting in this way for the flow of solids was considered by Tammann (*Ann. Phys.*, 1902, [4], vii., 198; "Krystallisieren und Schmelzen," Leipzig, 1903, p. 173), but summarily rejected by him on what appear to the writer to be insufficient grounds. In the first place he doubts the thermodynamic admissibility of the derivation of the formula for the lowering of equilibrium temperature by unequal pressure. In the second place, in his experimental work he was unable to detect any discontinuity in the rate of flow at the pressure indicated by the formula as the melting pressure at that particular temperature. To reason from this lack of discontinuity that the effect of unequal pressure upon the melting-point is illusory might be justifiable if Tammann had been dealing with a single crystal; but dealing as he was with a conglomerate of crystals, flow began whenever the pressure on any one of them exceeded the melting pressure under the particular conditions. Indeed, the behaviour of ice in this respect is precisely similar to that of the metals—a fact specifically noted by Tammann himself—the only difference being that the absolute values of the pressure are lower than for the common metals.

Tammann concludes (*loc. cit.*):—"From the work on the velocity of flow of crystalline substances it follows that the flow is not conditioned by a previous melting, but that the *plasticity, the reciprocal of the viscosity, is a property characteristic of the substance.*" In order to account for the fact that the velocity of flow, and hence the "plasticity," of ice increases very considerably with the pressure, it must be assumed that its viscosity diminishes greatly with pressure. This assumption may hold, for water at low temperatures and low pressures is an exception to the general rule that the viscosity of liquids is increased by pressure (R. Cohen, *Ann. Phys.*, 1892, xlv., 666; Hauser, *Ibid.*, 1901, v., 597); to the writer, nevertheless, it seems less forced to account for the flow by the aid of the argument advanced in this paper, namely, that flow is the result of a partial melting. On this basis we can readily see why increased pressure, which causes more ice to melt, and hence increases the amount of water present, should increase the plasticity. Moreover, so far as the writer has been able to ascertain, this explanation conflicts with none of the recorded observations on the flow either of ice or of any other substance. Indeed, it receives direct confirmation from some recently published work of Hess on the plasticity of ice (*Ann. Phys.*, 1911, xxxvi., 449); he

* From the *Journal of the American Chemical Society*, vol. xxxiv., No. 6.

found, as Tammann previously had also observed, that at a given temperature a considerable movement of the plunger takes place under a pressure much lower than that deduced thermodynamically (on the assumption that the pressure acts *equally* on both the ice and the water produced by the melting), and presents indisputable evidence that the ice in these circumstances had actually melted.

The mode of action outlined in this paper, besides accounting plausibly for the magnitude of some of the mechanical properties of metals, can also be adduced to explain observations on the structure of metal which has "flowed," or has been subjected to deformation of any kind. The process of "flow," or of deformation, of a metal is always accompanied, as we have seen, by a number of changes, among others by a "hardening" of the metal; this term is used to denote an increased resistance to stress, and is in one sense unfortunately chosen, for Faust and Tammann (*Zeit. Phys. Chem.*, 1911, lxxv., 118) have shown that in some cases the "hardness," as measured by the sclerometer, is not affected by the process of "hardening." Faust and Tammann, by microscopic observation of the specimens, were able to determine with a precision of about 1 per cent the pressure or tension required to produce the first permanent deformation of a number of metals, and found that this lower elastic limit is the same for pressure as for tension. Further, slow increase of pressure above the lower elastic limit causes this limit to recede to higher pressures, until finally an upper elastic limit, the flow pressure, is reached. This, again, shows that increase of pressure produces an increased rigidity of the metal, which is in accordance with the idea, first enunicated by Beilby, that the change in properties of metals on hammering, rolling, &c., is a direct consequence of the deformation which occurs during the process.

Now, these facts accord well with the argument of the present paper; for, exactly as in the case of the consolidation of loose snow to a block of ice, as soon as the stress reaches an appropriate value (the lower elastic limit), melting and flow into the interstitial spaces take place, with immediately subsequent re-crystallisation; this process continues until this flow is no longer possible (the upper elastic limit), whereupon increased stress produces rupture of the material. Now, the actual process of flow diminishes the volume of the spaces into which flow is possible, and to this extent diminishes the inequality of pressure acting on liquid and solid; hence it requires progressively higher pressures absolutely (though at the same temperature the same *excess* of pressure on the solid) to produce flow; in other words, the rigidity of the material is increased.

A phenomenon analogous in every respect to that observed by Faust and Tammann has been recorded by Bridgman (*Phys. Rev.*, 1912, xxxiv., 1) in some very recent work on the collapse of thick walled cylinders under high hydrostatic pressure. Bridgman found, namely, that with every successive application of pressure, yield is not resumed until the previous pressure maximum has been reached or exceeded; this behaviour is just what we should expect if flow is conditioned by a true melting.

It is important to observe, in passing, that uniform (hydrostatic) pressure is without *permanent* effect on the properties of metals. Thus, Faust and Tammann found that the elastic limit of metal which had been subjected to high hydrostatic pressure remains unchanged; while, as regards the physical properties (density, &c.), it is generally recognised that the only effect of hydrostatic pressure is a temporary change in these properties, which vanishes again whenever the pressure is removed. In all discussions of the effect of pressure therefore it is essential that we distinguish carefully between uniform and non-uniform compression, since their effects are so dissimilar.

It is a well-known fact that the resistance to flow of eutectics (which are always fine grained) is always greater than that of their components (see Note 15); further, that the varieties of steel possessing the greatest tensile strength (vanadium steels) are very fine grained. From the standpoint adopted in this paper one might reason that such metals are strong *because* they are fine grained; hence, if we wish to make a steel of high tensile strength, we should endeavour to obtain a very fine grained structure, producing this by whatever means (addition of foreign material, heat treatment, or mechanical treatment) may be found suitable for this purpose.

It was noted above that the deformation of metals is accompanied by the appearance of an "amorphous" phase, according to Beilby; by the production of smaller crystallites, according to Faust and Tammann. Neither author speaks definitely of the mode in which the change takes place, nor do they, as far as one can judge, consider it as a manifestation of real melting, with immediately subsequent re-solidification. When looked at in this way the divergence between their points of view disappears. For, as is well known, the size attained by a crystal depends, *ceteris paribus*, on its rate of formation; so that Beilby, with presumably a relatively rapid rate of re-crystallisation, obtained in his flowed metal crystals so small that the metal was apparently "amorphous"; Faust and Tammann, on the other hand, using a totally different method, in which the rate of re-crystallisation was presumably not so great, obtained relatively larger crystal particles.

A point worth mentioning in this connection is this, that the appearance of the cut and polished surface of a metal is not necessarily an altogether fair criterion of the structure of the massive metal. For, as Beilby has demonstrated conclusively, the process of polishing (and obviously of cutting also) is the result of flow; while in accordance with the viewpoint presented in this paper, flow is the result of a partial melting. Therefore, it is a safe assertion that between the apparent structure of the polished surface and the actual structure of the massive metal, there must always be some differences, which may be so large that examination of the surface only would lead to totally misleading conclusions with regard to the structure of the massive metal.

Kurnakov and Zhemzhuzhny (*loc. cit.*) made parallel measurements of the electrical conductivity and flow pressure of series of binary alloys, and found that for given binary systems minimum conductivity and maximum flow pressure occur at the same composition. This exemplifies the general rule that the conductivity of an alloy is less than that of its component metals. Moreover, the conductivity of a metal generally decreases when the metal undergoes deformation (*e.g.*, drawing to wire, hammering, or rolling). Now, if we interpret these facts with the aid of the idea that the specific conductivity of a given material diminishes progressively, other things being equal, with the size of the component particles—an idea which is substantially correct for powdered metals—we find them to be in complete harmony with the conclusion reached on other grounds, namely, that the size of grain of alloys or of metal which has been deformed is less than that of the pure annealed metals.

Summary and Conclusion.

In the foregoing pages we have discussed the idea that the "flow," or permanent distortion, of metals is conditioned by a real melting, not of the whole mass of metal at any one instant, but of successive groups of particles (namely, those on which the brunt of the strain momentarily falls); and have shown how this idea serves to correlate some properties of metals which at first sight would appear to bear no relation to each other. It leads, namely, to the fact that there is a parallelism between all the elastic properties of metals for which quantitative measurements have been made and the pressure—assumed to act on the solid phase, but not, or not to the same extent, on the liquid phase—which is required to lower the melting-point to ordinary temperature. This pressure is a function of the melting-point, latent heat of melting, and density at the melting-point of the metal; hence, if these quantities are known for any substance, we can predict

the relative order of magnitude of any of its properties which imply deformation of the material.

The same mode of reasoning is equally valid for any crystalline substance, and could be applied to all salts (including silicates and other geologically important substances) if the necessary data were available. At the present time, values of the latent heat of melting are few and far between, so that no general discussion of this part of the subject is practicable now.

The equation discussed in this paper cannot be applied to glasses; for since they are merely supercooled liquids, the value of Q is zero and hence dT/dP is infinite. But this is not so contradictory as at first sight it may seem; for glasses behave as liquids of exceedingly high viscosity, provided always that, comformably with this high degree of viscosity, sufficient time be allowed for the motion to take place.

In conclusion, let us give a brief indication of a connection between the relations discussed in this paper and the conception of "molecular vibration frequency," a conception which has been very fruitful in the hands of Nernst and Lindemann (see Note 16), Grüneisen (*Ber. Phys. Ges.*, 1911, 426, 591), and others. It has been established, namely, that a large number of apparently diverse physical properties of a substance—melting point, specific heats, coefficients of thermal expansion and compressibility, electrical resistance—may be considered to be functions of a characteristic quantity, the molecular "vibration frequency" (see Note 17).

Expressions containing this quantity have been derived by means of which the actually observed variation with temperature of certain of the above properties can be reproduced with remarkable accuracy. Now the flow pressure ϕ at the temperature t is determined by a complicated expression, the value of which depends upon t, T_1 (the ordinary melting-point), L (the heat of melting at T_1), V (the specific volume at T_1), and upon the variation of L and V with pressure and temperature; that is, for any particular substance, ϕ depends upon the above constant quantities and upon the specific heats and coefficients of thermal expansion and of compressibility; each of these quantities is some function of the "vibration frequency," consequently the flow pressure ϕ is also a function of this same characteristic parameter.

In view of the state of our knowledge (at the best, very approximate only at the present time) of the experimental data and of certain of the relations involved, it seems premature to endeavour to deduce a definite mathematical relation between them ϕ and the frequency, or even to determine the exact form of the function. The existence of such a relationship accounts simply for the parallelism between the calculated ϕ values (of Table I.) and the mechanical properties of metals brought together in Table II.; for all of these quantities are functions of the vibration frequency, a fact which indicates that all the mechanical properties of metals will be found to be periodic functions of their atomic weights, since the vibration frequency itself is doubtless such a periodic function.

Notes.

14. Beilby here uses the term "amorphous" to denote "a heterogeneous assemblage of molecules."

15. This was demonstrated conclusively by Kurnakov and Zhemzhuzhny (*Zeit. Anorg. Chem.*, 1908, lx., 1; 1909, lxiv., 149), who present results—in part from the literature, in part original—for a large number of alloys (and also for some pairs of organic substances) which demonstrate this fact. It has been further confirmed by Tammann, who recently (*Nachr. Ges. Wiss. Göttingen*, 1911, p. 181) described experiments with a few alloys, carried out in quite a different way, from which he draws the conclusions that this increased strength is a direct consequence of the fact that the alloys are finer grained than their components but offers no explanation as to why a fine grained conglomerate should be stronger than one composed of coarser particles); further, that the increased strength of metals which have been chilled is a direct consequence of the decreased size of the grains produced by rapid cooling of the melt.

16. This work has been published in a series of recent papers which have appeared in *Sitz. Akad. Wiss. Berlin*, *Ann. Phys. Zeit. Elektrochem.*, and *Phys. Zeit.*

17. For a discussion of the exact significance of this quantity, the reader may be referred, in addition to the papers cited above, to recent papers by Einstein in *Ann. Phys.*

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, March 26, 1914.

Sir William Crookes, O.M., President, in the Chair.

Papers were read as follows:—

"*Nature of the Tubes in Marsupial Enamel and Bearing upon Enamel Development.*" By J. H. Mummery.

"*Oxidation of Thiosulphate by certain Bacteria in Pure Culture.*" By W. T. Lockett.

In the course of investigations on the oxidation of thiosulphate on bacterial sewage filters, it was found that the oxidation was due largely to the presence of living organisms. Experiments were undertaken with a view to the isolation of the organism or organisms capable of bringing about this oxidation.

Active solutions on plating out with gelatin (G.P.B.) and agar (A.P.B.) showed approximately 100 organisms per cc. Several of the more predominating types of organisms in pure culture, isolated from the above plates, were unable to bring about the oxidation of thiosulphate.

Subsequently, it was observed that a bacteriological slide made of a loopful of an active solution showed proportionately a greater number of organisms per cc. than was indicated by the gelatin and agar plates of the same solutions. Further, the microscopic appearance of these—consisting mainly of one particular type—was very different from that of the organisms previously subcultured.

All attempts to grow the particular and characteristic organism on the usual media, *e.g.*, nutrient gelatin and nutrient agar, failed. Ultimately it was found on plating an active solution on a solid gelatin medium, without bouillon, but containing ammonium sulphate and thiosulphate, that a great number of minute, slow-growing, circular, non-liquefying, bluish white colonies were obtained.

Plates made with such a medium showed that active solutions contained 100 to 1000 times more organisms per cc. than was shown on gelatin and agar.

The organism isolated as above on inoculation into a solution of thiosulphate, containing ammonium sulphate and a small quantity of free tartaric acid, was found capable of oxidising thiosulphate to sulphate in the course of two to three weeks' incubation at 20° C.

Further work is in progress relating to the morphology and classification of the organism which is apparently one hitherto unknown.

"*Production of Anthocyanins and Anthocyanidins.*" By A. E. Everest.

The question of the production of Anthocyan pigments from the yellow pigments of the flavone and flavonol class is discussed.

Evidence is brought forward to show that the Anthocyan pigments must be regarded as reduction products of

flavone or flavonol derivatives, and that they are readily produced as glucosides from the glucosides of the yellow compounds without intermediate hydrolysis.

"*Variations in the Growth of Adult Mammalian Tissue in Autogenous and Homogeneous Plasma.*" By A. J. Walton.

"(1) *The Decomposition of Formates by* B. coli communis; (2) *The Enzymes which are concerned in the Decomposition of Glucose and Mannitol by* B. coli communis." By E. C. Grey.

(1) The object of the investigation was to determine how an organism which produced only a trace of gas from a formate and no gas from glucose when acting on these separately was able to produce gas abundantly from a mixture of the two.

An artificially selected strain of *B. coli communis* which now produced no gas from glucose was made to act upon a mixture of calcium formate and glucose. The CO_2 evolved was measured. From this the CO_2 equivalent to the acids produced from the sugar was deducted. The difference represents CO_2 from formate, but must be multiplied by two, since only half the CO_2 produced is evolved, as seen from the equation—

$$Ca(H.COO)_2 + H_2O = CaCO_3 + CO_2 + 2H_2.$$

The results obtained indicate that the addition of glucose increased the decomposition of formate at least twenty-fold.

The explanation of the cases where CO_2 is not produced (formate alone, glucose alone) is that decomposition is inhibited readily by excess of acid or of alkali. But with the mixture the conditions are ideal for maintaining neutrality. The acid produced from the sugar neutralises the alkali produced from the formate. The reactions are thus mutually helpful, and, moreover, either regulates the velocity of the other.

The application of the results is suggested in the use of formates in certain cases in the place of alkali for maintaining the neutrality of media. The method described would be of value also (1) As a surer test of the capability of an organism to decompose formates; (2) As a criterion whether a strain apparently producing no gas from glucose may have been recently derived from a gas-producing strain.

(2) The work aims at determining the number of separate enzymes concerned in the decomposition of glucose and mannitol by *B. coli communis*.

The method consists of a comparison of the ratios in which the various products are formed by the normal organism with the ratios in which they are formed by artificially derived strains.

According as the ratios are constant or vary it may be deduced that the products arise by the same or different enzymes.

The main products are lactic acid, alcoholic acetic acid, and formic acid or its cleavage products ($CO_2 + H_2$).

The only ratio found for both glucose and mannitol which proved constant on selection was—

$$\frac{\text{Alcohol} + \text{acetic acid}}{\text{Formic acid} \times 2} = \text{unity}.$$

From this it is concluded—(1) Alcohol and acetic acid are derived from a common parent substance, probably acetaldehyde; (2) This substance is formed by an enzyme which also produces formic acid.

This parent substance (intermediate substance B) is regarded as being produced together with formic acid from a hypothetical (intermediate substance A) which is itself an isomer of lactic acid.

The essential differences between the proportions of the products arising from glucose as compared to mannitol may be shown to be conditioned by the extra hydrogen in mannitol. These considerations have been embodied in a scheme to represent on a common basis the decomposition by *B. coli communis* of glucose and mannitol. Evidence has also been adduced indicating that the process of artificial selection herein referred to has led to the production of an organism deficient in reductase.

"*Description of a Strain of* Trypanosoma brucei *from Zululand.* Part I. *Morphology.* Part II. *Susceptibility of Animals.* Part III. *Development in* Glossina morsitans." By Surg.-General Sir D. Bruce, F.R.S., Major A. E. Hamerton, Captain D. P. Watson, and Lady Bruce.

"*The Trypanosoma causing Disease in Man in Nyasaland.* Part III. *Development in* Glossina morsitans." By Surg.-General Sir D. Bruce, F.R.S., Major A. E. Hamerton, Captain D. P. Watson, and Lady Bruce.

CHEMICAL SOCIETY.

Ordinary Meeting, March 19, 1914.

Prof. W. H. Perkin, LL.D., F.R.S., President, in the Chair.

(Concluded from p. 166).

83. "*The System Silver — Silver Sulphide.*" By Crellyn Colgrave Bissett.

The above system has been investigated both by thermal and by microscopic methods. From the results of the investigation it was concluded that:—(1) Silver and silver sulphide are only partially miscible in the liquid state. All alloys having an average composition between approximately 17 and 94 per cent of sulphide separate into two layers on being melted, and freeze at a constant temperature of 903°.

2. Silver and silver sulphide form a eutectic containing approximately 99 per cent of sulphide. The freezing-point of the eutectic was found to be 804°.

3. Silver and silver sulphide probably form solid solutions to some extent.

84. "*The Action of Sulphur on Amines.* Part II. *Aniline.*" By Herbert Henry Hodgson and Alfred Gilbert Dix.

The authors have studied the action of sulphur on aniline in the presence of its hydrochloride or hydrochloric acid. It is found that trithioaniline is produced in quantitative yield, and the previous discrepancies of other authors are to be explained by secondary actions between the trithioaniline, aniline, and sulphur. Although the free base itself could only be obtained in a resinous condition, the *sulphate*, *hydrochloride*, and *oxalate* have been prepared, together with the *benzoyl derivative*. The wool dye-stuffs obtained by diazotising the sulphate and combining with the usual components were found to be exceptionally fast to ordinary agents, and particularly so to milling. Iodine had the same influence as hydrochloric acid on the course of the reaction. On reduction the trithioaniline gives a dithioaniline, but the poor yield has led to an investigation of the mechanism of the reduction. Anomalies noticed when trithioaniline is condensed with *m*-nitrobenzaldehyde, and also when diazotised and coupled with β-naphthol, seem to indicate that one of the sulphur atoms is only loosely combined.

85. "*Investigations on the Dependence of Rotatory Power on Chemical Constitution.* Part VI. *The Optical Rotatory Powers of Methyl-*tert.*-butyl-, Methylbenzyl-, Methylphenylethyl, and Methyl-α-naphthylcarbinols.*" By Robert Howson Pickard and Joseph Kenyon. (This paper corresponds in part with the preliminary note published in *Proc.*, 1912, xxviii., 42).

The preparation of the optically active forms of these carbinols was described.

1-*Methyl-α-naphthylcarbinol* (m. p. 47°), when supercooled at the temperature of the laboratory, exhibits anomalous rotatory dispersion.

86. "*Salts which contain Two Solvents of Crystallisation.*" By James Ernest Marsh.

When the salt $KHgI_3,H_2O$ is added to methyl carbonate,

the clear yellow crystals crumble to a nearly colourless powder. On warming, all passes into solution, and on cooling the salt $KHgI_3,H_2O,3Me_2CO_3$ crystallises out. The ammonium salt $NH_4HgI_3,H_2O,2Me_2CO_3$ crystallises well. The rubidium salt $RbHgI_3,H_2O,2Me_2CO_3$ is also crystalline, but nearly insoluble in the solvent. A sodium silver iodide with water and methyl carbonate of crystallisation has also been obtained.

87. "*Menthyl Esters of Chloroacetic, Menthoxyacetic, and Methylalininoacetic Acids.*" By PERCY FARADAY FRANKLAND and FRED BARROW.

These compounds have been prepared by the authors in connection with their search for an optically active acid chloride which would be easily accessible and not liable to racemisation.

Owing to the great stability of the ester-grouping in menthyl chloroacetate, the authors find the latter to be a very convenient optically active compound from which to obtain derivatives by the interaction of the halogen-atom and other groups. Thus menthyl menthoxyacetate and menthyl methylalininoacetate were obtained by the action of sodium menthoxide and methylaniline respectively on menthyl chloroacetate. (Compare also the use made by P. F. Frankland and H. H. O'Sullivan of menthyl chloroacetate and menthoxyacetic acid, *Trans.*, 1911, xcix., 2325; 1912, ci., 287).

88. "*The Action of Thionyl Chloride on Lactic Acid and on Ethyl Lactate.*" By PERCY FARADAY FRANKLAND and WILLIAM EDWARD GARNER.

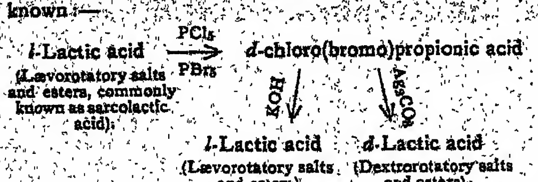
The authors direct attention to the apparent regularity in the action of thionyl chloride and silver oxide on optically active hydroxy-compounds. Four possibilities present themselves:—

$$\left.\begin{array}{ll} \text{I.} & l\text{-OH} \xrightarrow{SOCl_2} l\text{-Cl} \xrightarrow{Ag_2O} d\text{-OH} \\ \text{II.} & l\text{-OH} \xrightarrow{SOCl_2} d\text{-Cl} \xrightarrow{Ag_2O} d\text{-OH} \end{array}\right\} \text{Inversion.}$$

$$\left.\begin{array}{ll} \text{III.} & l\text{-OH} \xrightarrow{SOCl_2} l\text{-Cl} \xrightarrow{Ag_2O} l\text{-OH} \\ \text{IV.} & l\text{-OH} \xrightarrow{SOCl_2} d\text{-Cl} \xrightarrow{Ag_2O} l\text{-OH} \end{array}\right\} \text{No inversion.}$$

Only six hydroxy-compounds have hitherto been investigated in their relation to this pair of reagents, and in every case an inversion is effected, the transformation taking place according to scheme I. in the case of phenylglycollic acid (mandelic acid), α-hydroxy-α-phenylpropionic acid (atrolactinic acid), β-hydroxy-β-phenylpropionic acid, and phenylmethylcarbinol, and according to scheme II. in the case of malic acid and α-hydroxy-β-phenylpropionic acid, although for the latter compound the data are incomplete and somewhat obscure. Hitherto no transformations according to schemes III. and IV. have been observed.

The authors have completed the data bearing on lactic acid, for which the following transformations are already known:—



By the action of thionyl chloride the authors have found that—

$$d\text{-Lactic acid} \xrightarrow{SOCl_2} l\text{-chloropropionic acid}$$
(Dextrorotatory salts and esters).

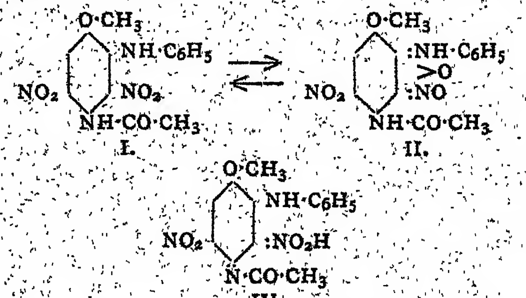
$$\text{Ethyl } d\text{-lactate} \xrightarrow{SOCl_2} \text{ethyl } l\text{-chloropropionate.}$$
(Dextrorotatory).

The transformations of lactic acid are, therefore, similar to those of malic acid, and take place according to scheme II. above.

A number of intermediate compounds were encountered in the action of thionyl chloride on the lactic acid and its ester. Thus, from the feebly active d-lactic acid (dextrorotatory salts and ester) employed there were obtained chlorosulphinyl-lactic chloride (very strong dextrorotation), chloropropionyl chloride (feeble dextrorotation), chloropropionic acid (lævorotation), ethyl chloropropionate (lævorotation), chloropropionyl-lactic chloride (dextrorotation), chloropropionyl-lactic acid (dextrorotation), ethyl chlorosulphinyl-lactate (very strong dextrorotation), and ethyl thionyl-lactate (very strong dextrorotation).

89. "*Synthesis with Phenol Derivatives containing a Mobile Nitro-group. Part VI. Substituted Alkyl- and Aryl-phenylamines: Colour in Relation to Tautomerism.*" By RAPHAEL MELDOLA and WILLIAM FRANCIS HOLLELY.

The authors have studied the action of primary and secondary amines on the 2 : 3 : 5 trinitroanisidine of Reverdin, and have obtained a series of alkyl- and aryl-phenylamine derivatives, all of which result from the replacement of the 2-nitro-group by the amine residue. Tertiary amines have no action. The compound obtained by the action of aniline, 3 : 5-dinitro-2-phenylaminoaceto-p-anisidide, exists in two differently coloured tautomeric forms which are interconvertible, and to which the authors assign the formulæ:—



One of these modifications is ochreous and the other red, the latter being regarded as an inner salt (II.) and the former as having the normal constitution (I.). Both forms dissolve in alkali with a yellow colour; the authors give reasons for believing that in alkaline solution configuration III. exists, this form reverting at once to I. when precipitated by acids.

90. "*A Formula by means of which the Molecular Volume at the Boiling-point may be Calculated.*" By GERVAISE LE BAS.

In an extended study of molecular volumes, it was found necessary to calculate some of the values at the boiling-point, and the following formula has been found suitable for this purpose:—

$$\frac{273}{\text{B. p.}} = \left\{1 - c\left(\frac{d_t}{d_0} - 1\right)\right\}.$$

The only data necessary are the density at 0° and the boiling-point.

The value of c is given in Table I., the data being those of Thorpe.

It is found that by means of the above formula the volumes of compounds of a similar order of complexity can be calculated to within 1 per cent.

Example.—$GeCl_4$, d_{18} 1·887 (Winkler), b. p. 86·0°; $\frac{253}{T} = 0{\cdot}771$; $\frac{d_0}{d_t} = 0{\cdot}46 \times 0{\cdot}229 = 1{\cdot}1053$, $d_{\text{b.p.}} = \frac{1{\cdot}887}{1{\cdot}105} = 1{\cdot}708$. M.W. = 213·8; M.V. 124·6.

Observed, C 14·8, Si 32, Ge [36·2], Sn 42·3, Ti [35·7].

The formula can be used indifferently for inorganic and organic compounds, but the value of c in the latter varies

TABLE I.—*Table of Values (Inorganic Compounds).*

Compound.	B. p.	d_0.	$d_{b.p.}$	c.	M.V. calc.	M.V. obs.	Per cent error.
$S_2O_5Cl_2$	139·6	1·85846	1·60610	0·460	135·5	135·5	±0·0
$SO_2Cl·OH$	155·3	1·78474	1·54874	0·420	75·5	75·05	+0·7
SO_2Cl_2	70·0	1·70814	1·56025	0·462	86·3	86·3	±0·0
$AsCl_3$	130·2	2·20500	1·91813	0·447	95·1	94·37	+0·76
AsF_3	60·4	2·6659	2·4497	0·490	53·6	53·84	−0·44
$VOCl_3$	127·2	1·86534	1·63073	0·452	106·5	106·2	+0·3
$POBrCl_2$	137·6	2·12065	1·83844	0·458	107·5	107·4	+0·1
$PSCl_3$	125·1	1·66820	1·45599	0·455	116·3	116·1	+0·2
$POCl_3$	107·2	1·71163	1·50967	0·474	101·0	101·4	−0·4
$TiCl_4$	136·4	1·76041	1·52223	0·460	124·5	124·5	±0·0
$SiCl_4$	57·6	1·52408	1·40494	0·500	120·2	120·8	−0·5
N_2O_4	21·6	1·49030	1·43958	0·473	64·0	63·9	±0·0
Mean value				0·463			

TABLE II.—*Cyclic Compounds.*

Compounds.	M. p. or 0°.	B. p.	d_t. 0° or m. p.	d_T. T=B. p.	c.	M.V. calc.	M. V. obs.	Per cent error.
C_6H_6 (benzene)	6·0°	80°	0·8940	0·8133	0·470	95·7	96·0	−0·03
C_4H_4S (thiophen)	0·0	84	1·0884	0·9874	0·434	85·5	85·0	+0·6
$C_{10}H_8$ (naphthalene)	79·2	217	0·9777	0·8674	0·456	147·3	147·2	±0·0
$C_{10}H_{14}$ (hexahydronaphthalene)	0·0	200	0·9419	0·7809	0·487	170·0	171·2	−0·7
$C_{14}H_{10}$ (phenanthrene)	100·5	340	1·0630	0·9073	0·440	197·8	195·2	+1·3
C_5H_5N (pyridine)	0·0	115	1·0033	0·8826	0·462	89·3	89·3	±0·0
C_9H_7N (quinoline)	0·0	234	1·1081	0·9211	0·439	141·1	140·0	+0·8
Mean value					0·460			

somewhat as the compounds vary greatly in complexity and the chains lengthen.

The value of c for organic cyclic compounds without side-chains is similar to the above. (See Table II.).

The results of calculation show very fair agreement with observation, and thus giving a fairly trustworthy method for the calculation of unknown values.

Example.—Hydrindene, C_9H_{10}: d_5 0·957, b. p. 176°, c = 46, M.V. 144·0. ΣnV_a = (4 × 9 + 10)3·7 = 46 × 3·7 = 170·2, Δ − 26·2 for ring. Contraction for 1 six-membered ring + 1 five-membered ring = −15 − 11·5 = −26·5.

Acenaphthene, $C_{12}H_8$.—The value of c for phenanthrene is 0·440. For acenaphthene, d_{103} 1·030, m. p. 103°, b. p. 277°. V_m 166·6, ΣnV_a 207·2, Δ = −40·6. Contraction for 2 six-membered rings + 1 five-membered ring = −30·0 − 11·5 = −41·5.

The only difficulty is met with in open-chain organic compounds. For compounds like chloroform, carbon tetrachloride, and trichloromethane, the value of c mentioned above (0·460) may suffice.

c, in general, increases by 0·024 for every addition of CH_2 in open-chain compounds, thus:—

C_5H_{12} 0·476, C_6H_{14} 0·500, C_7H_{16} 0·532, C_8H_{18} 0·554;
Δ 0·024 0·032 0·22

When considering an unknown value for a certain compound, it is usually possible to find an analogous compound from which c may be calculated, for example, cymene, $C_{10}H_{14}$, for the terpenes (menthane), $C_{10}H_{16}$, methyl succinate for methyl maleate or fumarate, propionitrile for ethyl carbylamine, and ethyl nitroethane for ethyl nitrite.

91. "*A Study of the Constitution of Nitrogen and Phosphorus Oxides and some of their Derivatives by means of Molecular Volumes.*" By GERVAISE LE BAS.

A study has been made of the above compounds by means of a new theory of molecular volumes, based on the original one of Kopp, or at least from his point of view. It recognises an additive principle, which is shown by the use of a system of atomic volumes, as follows:—C = 14·8, H = 3·7, O = 7·4 − 11·0, according to circumstances, S = 22·0 and 25·6, N = 15·6, P = 27·0. A number of constitutive features are also recognised. As a consequence, the constitutions of some of the above compounds are considered to be different from those usually accepted.

MISCELLANEOUS.

Method of Determining Glucinum.—André Kling and E. Gelin.—To determine glucinum mixed with oxides of aluminium and iron the hydroxides are first precipitated with ammonium chloride and ammonia, treated with nitric acid, and cautiously calcined. The residue is converted into acetates by means of pure acetic acid, and the mixed acetates are sublimed in a rarefied atmosphere containing acetic acid vapours. The basic acetate of glucinum is totally volatilised and is deposited on the cold parts of the glass tube in which the operation is carried out, while the basic acetates of aluminium and iron remain behind.—*Bull. de la Soc. Chim. de France*, No. 3, 1914.

Royal Institution.—A General Meeting of the Members of the Royal Institution was held on the 6th inst., The Duke of Northumberland, President, in the Chair. Miss A. R. Atkinson, Lady Esmonde, Mrs. H. J. F. Simson, and Mr. F. W. Goodenough were elected Members. The Chairman announced that the septennial award under the Acton Endowment had this year been made to Prof. C. S. Sherrington, Waynflete Professor of Physiology in the University of Oxford, for his important work entitled "The Integrative Action of the Nervous System," being a synopsis of his elaborate paper published in the *Philosophical Transactions of the Royal Society* on Experiments in Examination of the Peripheral Distribution of the Fibres of the Posterior Roots of some Spinal Nerves. Previous Actonian Awards have been made to Sir George Stokes, Miss Agnes M. Clerke, Sir William and Lady Huggins, and Mdme. Curie, for achievements in the field of physical science. Prof. Sherrington is the first investigator in Experimental Biology to receive this distinction for the third of a century.

MEETINGS FOR THE WEEK.

WEDNESDAY, 15th.—Microscopical, 8. "The Insect Pests of Wheat Crops," by F. Enock.

THE CHEMICAL NEWS.

VOL. CIX., No. 2838.

THE GENERAL BEHAVIOUR OF OPTICALLY ACTIVE COMPOUNDS AS REGARDS THE DEPENDENCE OF ROTATION ON TEMPERATURE, DILUTION, NATURE OF SOLVENT, AND WAVE-LENGTH OF LIGHT.*

By T. S. PATTERSON, D.Sc., Ph.D.

SOME twenty years ago the general opinion in regard to the influence of temperature on the rotation of an optically active substance probably was that the rotation, as in the case of a substance like ethyl tartrate, tended towards a constant value at higher temperatures, that the temperature-rotation curve became asymptotic to the axis of temperature. In 1896, however, it was shown by Frankland and Wharton (*Trans. Chem. Soc.*, 1896, lxix., 1587) in the case of ethyl dibenzoyl tartrate that a minimum rotation could exist, and some years later Winther (*Zeit. Phys. Chem.*, 1902, xli., 176), in an investigation connected with rotation-dispersion, fitted a parabolic expression to a number of temperature-rotation curves and made the assumption that since the parabola has a maximum, therefore the rotation of these substances should also pass through a maximum value. Somewhat later still the present writer showed that this maximum actually exists (*Trans. Chem. Soc.*, 1908, xciii., 1843), although at a different temperature from that deduced by Winther, and showed also that the maximum, instead of occurring at a constant temperature in a series of homologous compounds, or on dilution of an active substance with an indifferent solvent, moves gradually through a range of temperature. Thus, in nitrobenzene, for instance, the maximum rotation of ethyl tartrate, which occurs at a temperature of about 175°, moves rapidly towards a lower value as the solution becomes more dilute, the rotation, at the same time, becoming gradually greater. It thus becomes immediately clear why the rotation of a dilute solution of ethyl tartrate in nitrobenzene diminishes with rise of temperature, whilst the rotation of the ester itself and of its more concentrated solutions in nitrobenzene increases on heating; in the former case the ordinary temperature is on one side of the maximum, whilst in the latter case it is on the other. The temperature coefficients of all solutions of ethyl tartrate in nitrobenzene are less than that for the pure ester; nitrobenzene at the ordinary temperature has a powerful elevating effect on the rotation of this particular active compound. A number of other substances, however, of which acetylene tetrabromide may be taken as the best example, have an opposite effect. These substances have a considerable power to depress the rotation of the ester, and in agreement with this it is found that the temperature coefficient of all solutions made up of ethyl tartrate and that solvent have temperature coefficients which are greater than that of the pure ester. It may therefore be inferred that in these cases the maximum rotation would still persist but would move towards a still higher temperature, which in this particular case has not yet been actually observed. (Such evidence as exists in regard to this question will be found in a paper in the *Trans. Chem. Soc.* for 1913, ciii., 145; especially, perhaps, p. 171).

Further, it has been found that other solvents produce effects of a closely similar kind in such a way that if, for instance, a solution in water and one in nitrobenzene have one and the same rotation at some given temperature, then the temperature-rotation curves of the two solutions will be closely similar, although the concentrations may be entirely different. Thus the curve for a number of different solvents at various concentrations blend into a diagram remarkably like that for one single solvent at a number of concentrations, and it would seem as if we might almost eliminate from consideration the nature of the inactive solvent and the concentration, since the course of the temperature-rotation curve is apparently defined by the rotation at any given temperature (see Fig. 3, *Trans. Chem. Soc.*, 1908, xciii., 1846). When the influence of a particular solvent appears to be exhausted—that is, when its maximum influence has been reached in a dilute solution—the influence may be taken up, as it were, and carried on by another one more powerful. Thus α-nitronaphthalene, $p=55$, has approximately the same effect as nitrobenzene, $p=5$, so that the α-nitronaphthalene at $p=25$ appears to pick up the influence of the nitrobenzene at that point and carry it farther.

Another matter of interest in connection with the relation between temperature and rotation is the following. It has been found that certain substances, such as ethyl tartrate, show a maximum rotation, whereas some derivatives of that compound, for instance ethyl ditrichloroacetyltartrate, show on the contrary a temperature of minimum rotation, and a reconciliation of this exactly opposite behaviour must obviously present some difficulty. Possibly, however, the reconciliation may be effected in this way. It is known that the substitution of an alkyl radicle, such as *n*-propyl, *iso*-butyl, &c., for ethyl, in ethyl tartrate, moves the maximum rotation towards a lower temperature, whilst at the same time the actual value of the rotation is increased (*Trans. Chem. Soc.*, 1913, ciii., 148), and it seems reasonable to suppose that the very much greater change involved in the replacement of the hydroxylic hydrogen by the trichloroacetyl group should produce a correspondingly greater shifting of the temperature of maximum rotation. The maximum may, in fact, be shifted out of the region of ordinary temperatures altogether and the portion of the curve for the ditrichloracetyl derivative may correspond with some part of the graph for ethyl tartrate, a part with which we are unacquainted, only because we are not able at present to investigate the problem over a sufficient range of temperature. An examination of some of the data which have been obtained by various observers in the investigation of certain active substances over a fairly wide range of temperature strongly supports this view, for it is found that not only do maxima and minima exist in different curves, but that in the same curve not infrequently a maximum or a minimum together with a point of inflection may be observable.

No investigation has yet been carried out over a sufficient range of temperature to reveal both a maximum and a minimum. (This question has been fairly fully discussed elsewhere—*Trans. Chem. Soc.*, 1913, ciii., 151).

The temperature-rotation curve of an active compound is thus probably periodic, that is, may show several maxima and minima, and it seems probable that the influence of a solvent is simply to shift the complete curve of the homogeneous substance in one direction or another, but, of course, probably with minor alterations. Thus for ethyl tartrate the influence of nitrobenzene seems to be to shift the whole curve simultaneously towards a lower temperature and a higher rotation.

Rotation Dispersion.—Another very interesting question relates to the position of the maximum rotation for different colours of light. This is a subject which has been thoroughly investigated in only very few cases, but it would appear from the results which have been obtained that the maximum does not necessarily occur at the same temperature for different colours of light. Only two substances have been examined, ethyl tartrate and *n*-propyl tartrate, and in both the maximum rotation moves towards a higher temperature as the wave-length of the light

* Contribution to a General Discussion on "Optical Rotatory Power," held before the Faraday Society, March 27, 1914.

becomes less (*Trans. Chem. Soc.*, 1913, ciii., 165, 166). The temperature-rotation curve for violet light is thus apparently retarded on the temperature-rotation curve for yellow or for red light.

This is chiefly important in connection with what is called rotation dispersion. It is well known, of course, that the rotation of an active substance usually depends on the wave-length of the light used, and it is often stated that the rotation for violet light is greater than that for red. If, on the diagram showing the temperature-rotation curves for different colours of light in the case of ethyl tartrate, a vertical line be drawn through the temperature 160°, it will cut the temperature-rotation curves (*Trans. Chem. Soc.*, 1913, ciii., p. 165, Fig. 7) in the order violet, blue, green, yellow, red, and if these values be plotted on a new diagram relative to wave-length a graph will be obtained which is always, so far as the writer is aware, a curved line. If the line be drawn, however, at a temperature of say, 80°, it would cut the temperature-rotation curves in the order, blue, green, violet, yellow, red, and on plotting these values of rotation against wave-length a dispersion graph would be obtained rising from red to a maximum at blue and descending again to violet. Such a curve is generally said, without any proper reason, to be abnormal. At some wave-length intermediate between the extremes there is a rotation maximum. If now a line be drawn through the temperature -40° the sequence of the rotation values will be the same as at first, but the violet light gives the lowest rotation, a negative rotation being regarded as less than a positive rotation. This is, however, a purely accidental circumstance and is solely due to the fact that the temperature-rotation curves for ethyl tartrate happen to pass through the point of inactivity in the neighbourhood we are considering, otherwise the values for violet would be numerically less than for red. It is quite essential that in discussing rotation-dispersion some method must be devised which shall eliminate the sign of the rotation, and it would seem desirable to designate the dispersion on one sign of the region of intersection of these curves as positive and that on the other as negative.

The rotation-dispersion is often defined as the ratio of the rotations for various colours of light to the rotation for one given colour of light, such as red or yellow, but it has been carefully pointed out by Winther (*Zeit. Phys. Chem.*, 1902, xli., 205) that this is a very unsatisfactory procedure, giving most misleading values for rotation-dispersion as in the case of methyl tartrate. This point has been overlooked quite recently by Armstrong and Walker and by Pope and Winmill. The latter authors have measured the rotation, for three different lines of the spectrum, of derivatives of tetahydroquinaldine, and in regard to the -nitrobenzoyl derivative state that this substance exhibits quite abnormal rotation constants (*Trans. Chem. Soc.*, 1912, ci., 2311), whilst with regard to the 2-nitrotoluene-4-sulphonyl derivative they say (*loc. cit.*, 2316), "The considerable variation of rotatory dispersion of the latter substance with the solvent used is noteworthy."

Armstrong and Walker (*Proc. Roy. Soc.*, 1913, A, lxxxviii., 391) comment on what they term the abnormal dispersive power of these substances, and remark, "It is obvious that a special explanation is required to account for the peculiar behaviour of the two compounds mentioned." The rotatory dispersive power of these substances is, however, not more abnormal than is that of any of the other compounds examined by Pope and Winmill. The explanation, in the first case at least, is in fact purely arithmetical, the cause of any anomaly that exists being identical with that discussed by Winther in the case of methyl tartrate, already referred to; namely, that in certain of the solvents used, the rotation of the active compound passes through the point of inactivity, and that by applying an arithmetical process by a purely rule-of-thumb method to numbers sometimes negative and sometimes positive, one is bound to obtain quotients also sometimes positive and sometimes negative, but this merely indicates that the abnormality ought to be laid at the door of the substance examined.

The second of these two cases is, however, of considerable interest and will be referred to further on because it raises an interesting question in connection with normal rotation-dispersion, but before dealing with it we may revert for a moment to the case of ethyl tartrate in regard to abnormal rotation-dispersion. We have seen that at a temperature of about 80° the dispersion-rotation curve shows a maximum in the neighbourhood of the blue light, but that if the temperature be 160° there is no such maximum for these particular colours and that the same is the case if the temperature be about -40. To say, however, as is often done, that the rotation-dispersion at the high and low temperatures is normal whereas at the intermediate temperature it is abnormal seems very arbitrary. It must be clear that if both the other two curves were extrapolated so as to include the former case, light of wave-length considerably less than violet, a maximum would be very likely to appear in the curve, whilst at the low temperature of -40, if the rotation-dispersion curve were extrapolated, a maximum would occur, with equal probability, for light of greater wave length than red. The term abnormal, if it is to be used at all, should be applied, not merely to the temperature-rotation curve at one temperature, but to the temperature-rotation curves for all temperatures, in fact, to the substance itself. The reason for abnormal rotation-dispersion in the light of what has already been said as regards the maximum in temperature-rotation curves seems simple. The whole curve for violet light is retarded on that for blue, that for blue is retarded on that for green, and so on, the result being that the maximum passes to a higher temperature as the wave-length of the light decreases. In the same way, since the whole curve is displaced, and since, as appears to be the case, the sweep of these curves is the same also, they intersect one another at different points, not all at one point, and this gives rise to the phenomenon of anomalous rotation-dispersion.

It may be remarked in this connection that attention has often been drawn to the fact that abnormal rotation-dispersion occurs in substances the rotation of which alters rapidly with temperature-change. The reason for this seems clear from what has just been said. It is at a distance from a maximum—roughly speaking, midway between a maximum and a minimum—that rotation changes most rapidly with alteration of temperature, and it is just in this region that the temperature-rotation curves intersect and give rise to abnormal rotation-dispersion.

The question now arises, what is normal rotation-dispersion? or, to put it otherwise, do any substances exist which differ in their behaviour from ethyl tartrate? This is a question which cannot be settled at the present time, since, although a considerable amount of material has been collected, it scarcely touches the main question because the all-important matter of temperature-change has been left out of account. Nevertheless, very many statements may be found in the literature to the effect that this substance or that has normal rotation-dispersion, and the idea seems generally to be that if the dispersion coefficient varies comparatively little, perhaps when the compound is mixed with a solvent or when its temperature is altered slightly, then the rotation-dispersion is to be considered as normal. An example in which the temperature-change was very considerable is afforded by the dispersion data obtained by Pickard and Kenyon (*Trans. Chem. Soc.*, 1913, ciii., 1933). But it is, nevertheless, difficult to decide whether these substances really have normal rotation-dispersion or not. The matter may be considered in this way. It will probably be granted that the rotation of a substance for any colour of light varies at least to some extent as the temperature changes, as is the case, for instance, with the rotation of the alcohols prepared by Pickard and Kenyon. Now let us imagine that the rotation for a given substance for violet

light at a temperature t is A, and for red light is B, then the dispersion coefficent is A/B*; now suppose the temperature to change to t' and the rotation for violet light at this temperature to be A', and suppose that this is less than A, that is, that the rotation diminishes as the temperature falls, let us say, from t to t', then in order that the dispersion coefficient may be the same as before we must have $\frac{A'}{B'}=\frac{A}{B}$, B' being the rotation for the red light at the temperature t'. Now it will be obvious that this ratio can only be preserved provided the two temperature-rotation curves for violet light and for red light are such that they intersect at the point at which the rotation for both colours of light is zero, and that beyond the temperature at which this occurs they proceed again in a similar manner, but with negative, instead of positive, rotations. From such examples as we know it is impossible to decide whether this behaviour will be, in any way, general; whether temperature-rotation curves will cut in a single point just where the rotation is zero, and it seems to the writer that the apparent normality of certain rotation-dispersions is to be ascribed to the fact these dispersion coefficients have been measured on substances the temperature-rotation curves of which happen to have a maximum value in the neighbourhood of ordinary temperatures (as is the case with Pickard and Kenyon's alcohols), and are not due, or at least not necessarily due, to any inherent peculiarity of the substances themselves. But, of course, Pickard and Kenyon's alcohols may represent a class of substances conforming exactly to the type for which the temperature-rotation curves meet exactly at zero rotation.

Nevertheless, there is one point which may be considered, for it may, after all, be essential to distinguish between two different classes of compound. We have seen already that the family of temperature-rotation curves for a substance such as ethyl tartrate do not all cut in one point, and this, we have seen, was due to the fact that the maximum rotations for the different colours lie at different temperatures. Now it is quite possible that in certain other cases the maximum rotation for different colours of light may perhaps lie at the same temperature, in which case, if the sweep of the different curves were the same, the whole family of curves would cut in a single point, but of course it does not follow in any way that the rotation corresponding with the points in which they cut should be zero. No such instance as this has quite definitely been observed, but perhaps the data obtained by Pickard and Kenyon for optically active alcohols may represent a case of this sort which would account for the comparative constancy over a wide range of temperature of the dispersion coefficients, which happen to lie more or less in the neighbourhood of the maximum rotation. It is even more probable than the data already referred to, obtained by Pope and Winmill for 2-nitrotoluene-4-sulphonyl l-tetrahydroquinaldine, may be of the same sort. From a study of their data for this substance, it seems very likely that if a solvent could be found in which the active compound would have a rotation of about $-85°$ that the rotation would be identical at least for the three colours of light which they used, and perhaps it might be identical even for a wider range of colours than this.

These two classes of substances may be illustrated by two of the diagrams in the paper by Armstrong and Walker already referred to (*Proc. Roy. Soc.*, 1913, A, lxxxviii., 388). In that paper these authors have arrived at the conclusion that change of rotation, both with alteration of temperature and of solvent, is to be ascribed to a variation in the relative proportions of dynamic isomerides. Limitations of space render it impossible to point out the enormous objections which could immediately be brought against any such idea. It need only be remarked here that Armstrong and Walker's diagram on p. 398 is merely another method of representing rotation-dispersion, in which the values of the rotation are plotted relative to the rotation instead of relative to wave-length, and that they do not necessarily have anything whatever to do with the presence or absence of isodynamic isomerides. Since this diagram therefore merely represents dispersion data in a new way, the deductions which can be made from it are exactly those which could be made from ordinary dispersion-rotation curves, but inasmuch as the diagram depends upon a purely arbitrary assumption, it is of course of less value. It is to be noted that the lines for the different colours drawn on their diagram intersect practically at a single point, and that the diagram differs from those on p. 397 from methyl and ethyl tartrate exactly in this respect.

These two diagrams of Armstrong and Walker represent the same thing as is shown in the diagram Fig. 7 of a paper by the present writer for ethyl tartrate (*Trans. Chem. Soc.*, 1913, ciii., 165), where there is also an intersection of temperature-rotation graphs throughout a certain range. It may possibly be that substances really exist in two classes, those for which the temperature-rotation curves or Armstrong and Walker's dispersion curves cut in a single point and those for which they cut over a range of temperature or rotation, but this is likely to be the only difference which can be discovered in regard to rotation-dispersion between various active compounds. Whether it will be wise to label one as normal and the other as abnormal remains to be seen.

Only one further matter need be referred to, namely, rotation-dispersion in solution. It has been shown by the present writer that the temperature of maximum rotation of a substance such as ethyl tartrate moves to a different temperature as the concentration is varied. Very few substances have been examined for different colours of light in various solvents and at several concentrations, but it appears very clearly from the data which have been collected by Winther for tartaric acid in water and in alcohol, that the period of intersection of the temperature-rotation curves is very similar in solution to what it is for the homogeneous substance, and further, that on dissolving the compound in a liquid this period of intersection shifts its position on a diagram in exactly the same kind of way that the maximum rotation shifts its position (see *Trans. Chem. Soc.*, 1913, ciii., 167, Fig. 9). It seems, therefore, extremely probable, in fact it seems certain, that the so-called normality of the rotation-dispersion of, say, tartaric acid in water is solely to be ascribed to the fact that the influence of the solvent is to move the maximum of the temperature-rotation curves into the ordinary temperature, and at the maximum rotation the so-called dispersion coefficient appears to be normal. This greater normality is, however, altogether imaginary, since the abnormality has merely been shifted to a different region of temperature. It is for a similar reason that the rotation-dispersion of the alkali tartrates appears to be normal.

It may perhaps be mentioned in conclusion that by the adoption of the point of view advocated in this paper and in *Trans. Chem. Soc.*, 1913, ciii., 145, a survey of all the phenomena of optical activity may be made and a comprehension of the interdependence and interrelationship of these phenomena be obtained, and in addition it may be observed that this advantage is gained independently of any theory as to the ultimate causes of the phenomena discussed. The writer's own working hypothesis as to the mechanism of these changes has been detailed in various papers, and it is perhaps only necessary to say here that the statement by Pope and Winmill (*Trans. Chem. Soc.*, 1912, ci., 2313), which is prominently quoted by Armstrong and Walker (*Proc. Roy. Soc.*, 1913, A, lxxxviii., 390), to the effect "that he has abandoned the view that internal pressure is an operative factor in connection with variations in the rotatory power," is incorrect.

* This is the ordinary way of looking at the matter. Winther's method is much better, but for reasons which cannot be entered on here it also would probably fail if applied over a wide range of temperature.

A MODIFICATION OF THE USUAL METHOD OF CORRECTING SILICA FOR INCLUDED SALTS.

By S. B. KUZIRIAN.

When silica, liberated by the action of hydrochloric acid upon the product of fusion of a silicate with an alkali carbonate, is made insoluble and separated by the usual subsequent treatment—viz., evaporation, desiccation at 110°, extraction with dilute hydrochloric acid and water, filtration, and repeated washing with distilled water—it nvariably contains foreign material which, after strong ignition, consists essentially of oxides, free or combined with the silica. If the silica is volatilised by treatment with hydrofluoric acid and sulphuric acid, the included material is composed of sulphates which remain as such, or are changed to oxides in a subsequent ignition. If the constituents of this residue were definite and correctly determinable, it would be possible to calculate the weight of the oxides as they exist in the strongly ignited silica, and to make the proper correction; but it is a difficult task to make a correct analysis of a residue which sometimes does not exceed 2 to 3 mgrms., and may contain iron, aluminium, manganese, titanium, magnesium, sodium, potassium, &c. In order to avoid making the quantitative analysis of this small residue of sulphates and oxides, it has been an approved procedure to blast the silica to constant weight, and then to assume that after the prolonged blast ignition the impurities are left in the form of oxides. Then, after the removal of the silica with sulphuric and hydrofluoric acids, the remaining sulphate residue is also blasted to constant weight, and the assumption is made that this latter step will transform the sulphates of the residues into their oxides. The weight of silica is then found by difference. It will be shown in the following account of experimental work that the residue obtained after treatment of the blasted silica with sulphuric and hydrofluoric acids and blasting does not accurately represent the amount of included material as it is ordinarily weighed with the silica.

In the presence of moisture from the Bunsen burner or the blast-lamp, chlorides are slowly decomposed with evolution of hydrochloric acid and the simultaneous formation of metallic oxides, or, in the case of the alkali metals, hydroxides, which may then enter into combination with any suitable non-metallic oxide with which they are in contact. Silica containing traces of soluble alkali chlorides may, on strong ignition, gradually combine with the metallic oxides formed, as has been shown in a previous paper (*Am. Journ. Sci.*, 1913, xxxvi., 598). The assumption that the impurity in the silica, contaminated by chlorides when it is separated, consists after the ignition exclusively of oxides is therefore well founded.

Alkali sulphates, on the other hand, do not yield definite and weighable oxides on ignition. Moreover, they may volatilise as such at the high temperature of the blast-lamp. The experiments of Table I. show that the presence of silica does not materially change this characteristic of alkali sulphates, and that when a small amount of an alkali chloride is added in solution to ignited silica, and the mixture evaporated to dryness and treated with sulphuric acid, the residue left after ignition with the Bunsen burner is essentially the neutral sulphate.

Table I.

Silica ignited with Bunsen burner ½ hour.	Silica ignited with blast-lamp 20 mins.	Na_2SO_3 equivalent to NaCl added.	Increase in weight of silica after addition of NaCl, treatment with H_2SO_4 and ignition with Bunsen burner.	Error when the impurity is corrected as Na_2SO_4.
Grm.	Grm.	Grm.	Grm.	Grm.
0·4779	0·4776	0·0122	0·0131	+0·0009
0·5316	0·5315	0·0122	0·0131	+0·0009
0·5266	0·5264	0·0122	0·0122	—
0·5311	0·5293	0·0115	0·0115	—

That elements other than sodium and potassium, present originally with the silica as chlorides and converted to sulphates by the action of sulphuric acid and gentle ignition, may be recovered essentially as sulphates after treatment with sulphuric and hydrofluoric acids and gentle ignition, is shown in Table II.

Table II.

Silica ignited with Bunsen burner ½ hour.	Silica ignited with blast-lamp 20 min.	Sulphate equivalent to chloride added.	Sulphate determined by increase in weight of silica.	Sulphate left after removing silica by H_2SO_4+HF.
Grm.	Grm.	Grm.	Grm.	Grm.
		$BaCl_2$ *added.*		
0·5290	0·5290	0·0103	0·0098	0·0104
		$CaCl_2$ *added.*		
0·5576	0·5572	0·0121	0·0114	0·0118
0·5351	—	0·0242	0·0218	0·0226
0·5486	—	0·0242	0·0242	0·0234
0·5413	—	0·0242	0·0228	0·0234
0·5486	0·5486	0·0242	0·0242	—
		$MgCl_2$ *added.*		
0·5441	0·5436	0·0200	0·0195	0·0197
0·5446	—	0·0200	0·0215	0·0220
0·5456	0·5456	0·0200	0·0203	—
		$AlCl_3$ *added.*		
0·5456	—	0·0195	0·0200	0·0195
0·5447	—	0·0195	0·0192	0·0205
0·5490	0·5490	0·0195	0·0188	—

As is well known, sulphates other than alkali sulphates lose the acidic oxide, more or less according to the conditions, when submitted to ignition with the blast-lamp. While prolonged blast-ignition may bring about a complete transformation of the sulphates of iron, aluminium, chromium, and titanium to the respective oxides, the refractory alkali sulphates, as well as the sulphates of magnesium, calcium, and barium in large degree, will remain in the condition of sulphates (though the alkali sulphates may volatilise appreciably), and the correction for silica as ordinarily applied will be in error by an amount approximately equal to that of the sulphur trioxide combined in the sulphates.

The source of error, inherent in the usual method of applying corrections to the ignited silica, may be largely avoided by the introduction of a slight modification of the treatment. This modification consists essentially in treating the ignited silica with sulphuric acid, gently igniting again before weighing, and in igniting under exactly the same conditions the sulphate residues left after the removal of the silica in the usual way. That is to say, the included impurities of the silica must be transformed before weighing into the condition in which they will be left when the silica is removed by sulphuric acid and hydrofluoric acid. This can be accomplished by adding a few drops of dilute sulphuric acid to the well ignited impure silica, evaporating the excess of the acid slowly over a radiator, and igniting the residue by means of a Bunsen burner, before weighing the residue. Then, after the removal of the silica in the usual manner, the sulphate residue left is ignited at the same temperature and for the same duration of time as was the silica, and then weighed. From the weight of the silica plus the impurity before the treatment with sulphuric acid and hydrofluoric acids, and that of the residue after that treatment, the weight of the silica is found by difference.

Table III. contains the details of experiments in which silica was fused with six times its weight of sodium carbonate, the melt treated with hydrochloric acid, the mixture evaporated, the residue desiccated, at 110° (A), or, in presence of acetic anhydride, at 137° (B), and extracted as usual with hydrochloric acid, the precipitate filtered off

and washed, and the filtrate treated again like the original solution of the melt for the recovery of silica soluble in the former operation. The residues (first, second, and total), and the error which results from calling these residues oxide instead of sulphate and subtracting their weight from that of the ignited silica, according to the usual method of making the correction, are shown.

TABLE III.

SiO_2 (blasted) taken.	Residue left by H_2SO_4+HF treatment of first precipitate.	Residue left by H_2SO_4+HF treatment of second precipitate.	Sum of residues.	Error which results from calling the residues oxide instead of sulphate.
Grm.	Grm.	Grm.	Grm.	Grm.
A.—*Desiccation at* 110°.				
0·5302	0·0010	0·0012	0·0022	+0·0013
0·5211	0·0010	0·0010	0·0020	+0·0012
0·5440	0·0010	0·0012	0·0022	+0·0013
0·5351	0·0010	0·0002	0·0012	+0·0007
0·5436	0·0010	0·0013	0·0023	+0·0014
B.—*Desiccation at* 137° *in Acetic Anhydride*.				
0·5520	0·0010	0·0003	0·0013	+0·0008
0·5452	0·0010	0·0010	0·0020	+0·0012
0·5347	0·0010	0·0005	0·0015	+0·0009
0·5521	0·0010	0·0005	0·0015	+0·0009

These errors, which are not inappreciable, were found when the silica was separated, as well as possible, from sodium chloride alone. When chlorides of other elements, such as magnesium, calcium, and aluminium, are present, the silica separated is likely to be also contaminated with these salts, which, by the ordinary treatment, will be transformed to oxides when the silica is ignited and to sulphates when the silica is removed, and these sulphates will be more or less refractory under ignition, according to their natures and to the duration and temperature of the ignition. The errors shown above for the case in which sodium chloride is the only contaminating salt are likely to be magnified in the analysis of ordinary silicates of complex composition. The proposed modification of treatment will therefore lead to a more accurate application of the correction for impurities included in the silica. In this procedure it is not necessary to blast either the silica or the residue before and after the removal of silica as silicon fluoride. The Bunsen burner will give a temperature sufficiently high to volatilise the excess of sulphuric acid, and to break up the acidic and pyrosulphates of the alkali elements. The included salts being weighed as sulphates, or as sulphates broken up to practically the same extent in both ignitions, the correction to be applied will be reasonably accurate.—*American Journal of Science*, xxxvii., p. 61.

A NOTE ON THE PREPARATION OF TELLURIC ACID AND A TEST FOR ASSOCIATED TELLUROUS ACID.

By PHILIP E. BROWNING and H. D. MINNIG.

Of the various methods suggested for the preparation of telluric acid, two only seem to be in general use:—First, the oxidation of tellurous acid by chromic acid (Staudenmaier, *Zeit. Anorg. Chem.*, x., 189; Gutbier, xxix., 22), and the precipitation of the telluric acid by nitric acid after the concentration of the solution; and second, the oxidation of an alkali tellurite by hydrogen dioxide, followed by the precipitation of the telluric acid by nitric acid (Gutbier, *Zeit. Anorg. Chem.*, xl., 260). While both of these methods give quite satisfactory yields, the difficulty of washing out the chromium salt in the first method (Kothner, *Annalen*, cccxix., 39), and of removing the alkali salt in the second method is apparent. Berzelius formed tellurates by passing chlorine into an alkaline solution of a tellurite, but here also the precipitation of the telluric acid would have the same disadvantage in the inclusion of alkali salts.

The work to be described was undertaken to study the effect of free chlorine upon elementary tellurium suspended in water. The element in the form of an amorphous powder weighing several grms. was suspended in water and subjected to the action of a current of washed chlorine gas. After about an hour the tellurium had dissolved, and a portion of the solution, made alkaline and then acidified with acetic acid, remained clear, showing the complete oxidation to telluric acid.

It was found by experimentation with solutions of tellurates and tellurites that this method of testing would detect a mgrm. of tellurous acid in the presence of between 100 and 200 mgrms. of telluric acid, in a volume of 5 cc.

When the solution was thoroughly saturated with chlorine and the complete oxidation was shown by this method of testing, the solution was evaporated to small volume, tested to be sure that no reduction had taken place, and again treated with chlorine if necessary. The concentrated solution was then treated with acetone or ethyl alcohol to the complete precipitation of a beautifully crystalline product of satisfactory yield. This product was washed with acetone or alcohol until the washings gave no test with silver nitrate for hydrochloric acid.

The telluric acid obtained was readily soluble in water; moreover, the solution gave no indication of the presence of tellurous acid on treatment with an alkali hydroxide and acetic acid, and was not reduced by stannous chloride except on warming.

After concentration of the telluric acid solution, the acid may be precipitated by nitric acid, washed with the same reagent to remove the hydrochloric acid, and then with acetone or ether to remove the nitric acid. This modification of the process, however, appeared to have no advantage in the purity of the product.

The absence of contaminating salts is practically assured by the method described if the elementary tellurium used is reasonably pure.—*American Journal of Science*, xxxvi., p. 72.

THE USE OF THE AMMONIUM SALT OF NITROSOPHENYLHYDROXYLAMINE ("CUPFERRON") IN THE QUANTITATIVE SEPARATION OF TITANIUM FROM IRON.*

By WILLIAM M. THORNTON, Jun.

NITROSOPHENYLHYDROXYLAMINE was first synthesised by Wohl (*Ber.*, 1894, xxvii., 1435). The ammonium salt of nitrosophenylhydroxylamine was brought into service in analytical chemistry by Baudisch (*Chem. Zeit.*, 1909, xxxiii., 1298) for the estimation of either copper or iron, the separation of these two metals from various others, and indirectly for the separation of the former from the latter. Owing to these properties the trivial name of "cupferron" has been applied to the ammonium salt of nitrosophenylhydroxylamine. The analytical data given by Baudisch are few and not absolutely confirmatory. Since then, however, various other workers (notably Biltz and Hödtke, *Zeit. Anorg. Chem.*, 1910, lxvi., 426; Hanus and Soukup, *Ibid.*, 1910, lxviii., 52; and Fresenius, *Zeit. Anal. Chem.*, 1911, l., 35) have thoroughly demonstrated the value of this reagent for the quantitative precipitation of either copper or iron and their separation from various other bodies. In connection with other work, Schroeder (*Zeit. Anorg. Chem.*, 1911, lxxii., 89) has made the statement (*loc. cit.* p. 95) that titanium and zirconium could be quantitatively precipitated from their acid solutions by the "cupferron" reagent, and that experiments were in progress for the

* From the *American Journal of Science*, vol. xxxvii., p. 173.

estimation of these two elements. Schroeder, however, gave no experimental data, and has not published further upon the subject. Bellucci and Grassi (*Gazetta Chimica Italiana*, 1913, Anno xliii., parte I., 570) have shown that from solutions, moderately acidified with either sulphuric or hydrochloric acid, titanium could be quantitatively precipitated by the "cupferron" reagent, and that titanium could also, under these conditions, be quantitatively separated from aluminium. Under these circumstances the titanium comes down as a very bulky, readily filterable, precipitate of canary yellow colour. In the opinion of the aforesaid authors the precipitate, after having been crystallised from ethyl alcohol, is the titanic salt of nitrosophenylhydroxylamine, corresponding to the formula—

$$\left[\begin{array}{l} C_6H_5{-}N{=}N{-}O{-} \\ \qquad\ \ \| \\ \qquad\ \ O \end{array}\right]_4 Ti.$$

It has been known for a long time that certain organic acids, containing both hydroxyl and carboxyl groups, such as tartaric acid and citric acid, have the power to prevent the precipitation of certain metals when their solutions are made alkaline with sodium or potassium or ammonium hydroxide. This principle was made use of by Gooch (*Proc. Am. Acad. Arts and Sci.*, n. s., vol. xii., p. 435; CHEM. NEWS, lii., 55, 68) for the separation of titanium from iron; for, if the solution contain sufficient tartaric acid, the iron can be precipitated by ammonium sulphide as ferrous sulphide, and the titanium will then be found entirely in the iron free filtrate. The next step is to oxidise the tartaric acid; for titanium is not precipitated in its presence by any of the reagents previously used for its gravimetric estimation. This was accomplished by Gooch (*loc. cit.*, p. 445), after strongly acidifying with sulphuric acid by adding potassium permanganate to the boiling aqueous solution. This process is open to the objection that a great deal of manganese is thus introduced into the solution and is co-precipitated in some measure when the titanium is subsequently thrown down by hydrolysis of titanic acetate. A second precipitation is therefore necessary, which must be preceded by fusion with an appropriate flux and solution of the melt in acid. The author's experiments show that, after acidifying the filtrate from the ferrous sulphide, the titanium can be quantitatively precipitated by the "cupferron" reagent, notwithstanding the presence of tartaric acid.

Two solutions of titanic sulphate were employed for these experiments; which were prepared by warming potassium fluotitanate with concentrated sulphuric acid until all the hydrofluoric acid had been volatilised, pouring into cold water, and making up to known volume. The quantity of sulphuric acid used was such that the resulting solution contained about 10 per cent of absolute acid. In the case of the second solution, the trace of platinum was removed by saturating the solution with hydrogen sulphide, filtering off the platinic sulphide, boiling out the hydrogen sulphide, filtering again, and making up the solution to definite volume. The first solution was standardised by taking weighed portions of 25 cc. and precipitating the titanium by hydrolysis of the acetate. The solution was made nearly neutral with re-distilled ammonium hydroxide—until a faint permanent turbidity appeared. One cc. of a strong solution of ammonium hydrogen sulphite was added, followed by 15 grms. of ammonium acetate and 20 grms. of glacial acetic acid, and the solution made up to 400 cc. This solution was brought rapidly to boiling and maintained in ebullition for one minute. The precipitate was washed twenty times—first with boiling 5 per cent acetic acid, and finally with boiling water. In the usual manner the precipitate was ignited to titanic oxide and brought to constant weight over the Meker burner. Duplicate determinations gave the following results:—

Titanic sulphate solution.	Titanic oxide.	
(a) 25 cc. = 37·308 grms.	0·1427 grm.	0·5226 per cent
(b) 25 cc. = 27·319 grms.	0·1428 grm.	0·5227 per cent

Since these two values agreed so closely, (b) was arbitrarily taken as correct. The second solution was standardised by taking two weighed portions of 25 cc. and 24 cc. respectively and determining the titanium in one (a) by the acetate method given above, and in the other (b) by "cupferron" method of Bellucci and Grassi (*loc. cit.*) (the exact technique of which will be given presently). Duplicate determinations gave the following results:—

Titanic sulphate solution.	Titanic oxide.	
(a) 25 cc. = 27·814 grms.	0·1066 grm.	0·3832 per cent
(b) 24 cc. = 26·667 grms.	0·1022 grm.	0·3832 per cent

Since these two determinations agreed exactly, the value here obtained was taken as correct.

A solution of ferric sulphate was prepared by dissolving Baker's analysed ferric ammonium sulphate in water, adding 25 cc. of concentrated sulphuric acid per litre to prevent the formation of basic salt, filtering, and making up to definite volume. In one portion (a) of 25 cc. the iron was determined by titration with potassium permanganate after reduction by zinc—the potassium permanganate having been previously standardised against sodium oxalate. (The sodium oxalate was obtained from the Bureau of Standards, Washington). In another portion (b) of 25 cc. the iron was determined by precipitation with re-distilled ammonium hydroxide in a platinum basin and ignition of the precipitate to ferric oxide. Parallel determination gave the following results:—

Ferric sulphate sol ition.	Titanic oxide.
(a) 25 cc.	0·2267
(b) 25 cc.	0·2269

The value obtained in (a) by the volumetric method was arbitrarily taken as correct.

The supply of "cupferron" for these experiments was prepared in this laboratory according to the directions given by Baudisch (*Chem. Zeit.*, 1911, xxxv., 913). An approximately 6 per cent solution of the salt was made by dissolving it in cold water and filtering from any insoluble residue that remained.

The first series of experiments was carried out with a view to ascertaining whether or not titanium could be completely precipitated and accurately determined in the presence of tartaric acid. To a solution containing a known quantity of titanium a little more than three times the weight of the titanic oxide present was added of tartaric acid. The solution was made neutral to litmus with ammonium hydroxide, then acid again with 5 cc. of sulphuric acid (made by diluting acid of sp. gr. = 1·84 with an equal volume of water), and the volume made up to 200 cc. A little more than the calculated amount of "cupferron" solution was added, and the beaker set aside for the precipitate to settle. The supernatant liquid was tested by adding a few drops of the reagent, which were made to run down the wall of the beaker. The formation of a white precipitate of nitrosophenylhydroxylamine indicates that the reagent has been added in excess, while the formation of a yellow turbidity shows that the titanium had not been comptetely thrown out. It is well also to test the filtrate. The precipitate was filtered on paper, using very gentle suction, and washed twenty times with cold water. During the washing the suction should be almost stopped to prevent the wash water from running through too fast to accomplish much solvent work. The precipitate is very prone to develop mud cracks, and should therefore be agitated with the stream of water from the wash-bottle as much as possible. After having been sucked free from drainage water, the precipitate along with the filter was placed in a tared platinum crucible, dried at 110° C., very carefully heated until the volatile products of destructive distillation had escaped, the inclined open crucible ignited till all carbon had been consumed, and finally brought to constant weight over the Meker burner. If it is desired to save time, the precipitate can be dried by inclining the crucible, supporting the lid tongue downward on the triangle and edge of the crucible, and applying a

small flame beneath the lid. The heat is thus deflected downward, and the precipitate gradually dried from above with little danger of spattering (see Treadwell, "Analytical Chemistry," 1910, translated by Hall, vol. ii., p. 29). It is inadvisable to dry the precipitate in the funnel; for at a low temperature the substance melts, or at least assumes a plastic condition, and penetrates the pores of the filter; moreover, the dried material is very brittle, and on attempting to fold the paper and introduce it into the crucible particles are likely to fly away and be lost. In experiments (1) and (4) the filtration was carried out on asbestos in the perforated platinum crucible. Due to the above mentioned property, a little titanic oxide was found on the outer surface of the crucible after ignition. This method of filtration was therefore abandoned. Table I. contains the results of three experiments:—

Table I.

No.	TiO_2 taken. Grm.	TiO_2 found. Grm.	Error. Grm.	Tartaric acid. Grm.
1.	0·1428	0·1426	−0·0002	—
2.	0·1428	0·1429	+0·0001	0·5
3.	0·1066	0·1063	−0·0003	0·4

In the second series of experiments actual separation of titanium from iron was carried out. To facilitate the reduction of the iron the solution, to which tartaric acid equal to three times the weight of the titanic oxide and ferric oxide present had been added, was neutralised by ammonium hydroxide, 1 to 2 cc. of sulphuric acid (1 : 1) added, and the volume made up to about 100 cc. Hydrogen sulphide was then introduced till the solution appeared colourless. If the iron is not thus reduced before its precipitation, titanium will be thrown down in part also (A. Cathrein, *Zeit. Kryst.*, 1882, vi., 243; 1883, vii., 250). The solution was then made ammoniacal and more hydrogen sulphide introduced until the iron had been completely precipitated as ferrous sulphide—leaving the solution, however, alkaline to test-paper. The ferrous sulphide was filtered off and washed ten times with very dilute colourless ammonium sulphide. The filtrate was acidified with 25 cc. of sulphuric acid (1 : 1), the hydrogen sulphide boiled out, the acid partially neutralised with ammonium hydroxide so as to leave about 2·5 cc. of sulphuric acid (1 : 1) for every 100 cc. of the solution, and the "cupferron" added in the cold. Table II. contains the results of four experiments.

Table II.

No.	TiO_2 taken. Grm.	Fe_2O_3 taken. Grm.	TiO_2 found. Grm.	Error. Grm.
4.	0·1428	0·2267	0·1424	−0·0004
5.	0·1428	0·2267	0·1430	+0·0002
6.	0·1066	0·2267	0·1068	+0·0002
7.	0·1063	0·2267	0·1061	−0·0002

In the third series of experiments the solution containing the titanium and iron was divided into two aliquot parts by weight. In one part the titanium was determined by the method already outlined. In the other part the iron was determined by the method of Gooch and Newton (*Am. Journ. Sci.*, 1907, xxiii., 365). Table III. contains the results of two experiments.

Table III.

No.	TiO_2 taken. Grm.	Fe_2O_3 taken. Grm.	TiO_2 found. Grm.	Fe_2O_3 found. Grm.	Error TiO_2. Grm.	Error. Fe_2O_3. Grm.
8.	0·0716	0·1130	0·0719	0·1130	+0·0003	0·0000
9.	0·0717	0·1129	0·0716	0·1135	−1·0001	+0·0006

From the work of Bellucci and Grassi (*loc. cit.*), Fresenius (*loc. cit.*, and the author, it would seem that there should be no great difficulty attending the separation of titanium from iron, aluminium, and phosphoric acid, which are the substances with which titanium is commonly associated in nature. Experiments are now in progress by the writer for accomplishing this separation with the aid of the "cupferron" reagent, and the results will appear later.

ON THE PREPARATION OF TELLUROUS ACID AND COPPER AMMONIUM TELLURITE.

By G. O. OBERHELMAN and P. E. BROWNING.

Occasion having arisen to prepare some tellurous acid from residues from the electrolytic refining of copper (furnished through the kindness of the Baltimore Copper Co.), residues containing a high percentage of tellurous oxide together with small amounts of silica, copper, selenium, and several other impurities, it was determined to try the effect of the solvent action of ammonium hydroxide, followed by the precipitation of the tellurous acid from the ammoniacal solution by acetic acid. This procedure, employed on another occasion for the removal of selenium (Browning and Flint, *Am. Journ. Sci.*, 1909, [4], xxviii., 112), proved satisfactory for the removal of the greater part of the silica and of those bases which are insoluble in ammonium hydroxide. By dissolving the tellurous acid thus obtained in sodium hydroxide and precipitating the tellurous acid again by acetic acid, copper and many other metals whose hydroxides are insoluble in sodium hydroxide were also removed.

If the precipitation of the tellurous acid by acetic acid is brought about without warming the solution, and the product is dried without heating, the tellurous acid obtained is readily soluble in the alkali hydroxides. If, however, the precipitation takes place in hot solution and the precipitate is dried by application of heat, the product tends to be quite insoluble in the alkali hydroxides.

After the first treatment of the residues with ammonia in this extraction process, it was observed that a purple crystalline salt separated from the alkaline solution on standing. The colour suggested a copper compound, and after the removal of this salt by filtration, the filtrate proved to be practically free from copper. It was found that a salt similar in appearance could be produced by allowing an ammoniacal solution of tellurous acid containing some copper salt to evaporate over sulphuric acid and in the presence of soda-lime. The depth of colour varied with the concentration of the copper solution from a reddish purple through pink to nearly white. It was found that a salt which appeared to be identical with the compound just mentioned could be produced by adding slowly, with constant stirring, acetic acid to an ammoniacal solution of tellurous oxide and copper chloride. The precipitate thus obtained proved to be slightly soluble in water but insoluble in acetic acid and in 50 per cent alcohol. A sample of this compound prepared in the manner just described, which from its intensity of colour was considered to contain the maximum amount of copper, gave the following analysis:—

TeO_2	83·84
CuO	4·63
NH_3	5·22
H_2O	6·10
	99·79

The TeO_2 was determined by the permanganate method. Copper was estimated colorimetrically by comparing in Nessler tubes ammoniacal copper solutions of known strength with weighed amounts of the compound dissolved in acid and made ammoniacal. This method was found to be accurate to 2/10ths of a mgrm. The ammonia was determined by distillation from an alkaline solution into standard acid. The water could not be determined by difference on ignition owing to a slight reduction of the tellurium. So the compound was heated at 140°, and the residual ammonia was determined after weighing. From the weights of the total ammonia and of the residual ammonia at 140°, together with the total loss on heating at 140°, the weight of the water was determined. The loss of ammonia which resulted from heating at 140° proved to be about constant and amounted to a third of the total

ammonia. The colour of the substance changed on heating at 140° from reddish purple to blue.

It was thought that compounds of a similar nature containing bases other than copper might be formed in a similar manner. Nickel, cobalt, zinc, cadmium, and silver were tried, but with no success. Silver gave a yellow precipitate, but this proved to be the ordinary silver tellurite. —*American Journal of Science*, xxxvi., p. 299.

ERRORS IN GAS ANALYSIS DUE TO ASSUMING THAT THE MOLECULAR VOLUMES OF ALL GASES ARE ALIKE.*

By GEORGE A. BURRELL and FRANK M. SEIBERT.

Introduction.

The Bureau of Mines in the course of various investigations has sampled and analysed the gases found in coal and metal mines, those that flow from wells in oil and gas-fields, and those produced during the processes of combustion in furnaces. In determining the purity of certain combustible gases by the method of slow combustion, the authors found that in some analyses the volume of carbon dioxide and the contraction produced by the combustion did not agree with the theoretical value, according to the equations ordinarily used for showing the reaction. Also, in analysing some natural gases by the same method the paraffin hydrocarbons present totalled over 100 per cent. The differences were greatest when the oxygen taken was only a few cc. in excess of that required to burn the gas completely. The variations could not be attributed to experimental errors, because all the analyses were carefully performed in duplicate, and the gas burettes were accurately calibrated. Consequently, an inquiry was made to determine the errors that might arise in the combustion method of analysis, by assuming that the molecular volume (the quotient of the molecular weight divided by the density) is the same for every gas. This paper presents the results of that inquiry, and is published by the Bureau of Mines because these results show the need of applying corrections in some exact analyses of certain gases by the combustion method.

In working out the results, the authors wish to acknowledge the valuable assistance of G. A. Hulett, chief chemist of the bureau.

Deductions of Wohl and Haber.

Wohl has shown that the errors due to the assumption stated are considerable ("Calculation of Gas Analysis by Combustion," *Ber.*, 1904, xxxvii., 429), but the authors of this paper are not entirely in accord with some of his deductions. Wohl derives expressions for the molecular volumes from determinations taken from a table given by Nernst ("Theoretical Chemistry, 2nd Edition, 1898, p. 44). These values agree closely with the latest determinations except in the case of methane. The value for methane is given as 1·002 at 0° C. and 760 mm. Baumé and Perrot found it to be 0·999, as shown in the table of specific gravities (Table III., *prox.*).

Wohl's gas-analysis apparatus differs from the one used in the work herein reported in that his measurements were made at constant volume instead of constant pressure. Wohl made the mistake of assuming that the expressions he derived as showing the exact proportions of certain gases entering into reaction with each other could be used in all cases. The fact is that his equations apply only when the carbon dioxide produced by the combustion constitutes between 95 and 100 per cent of the total quantity of gases remaining after combustion. It is true, as he stated, that in the case of hydrogen, carbon monoxide, and methane the quotient of the molecular weight divided by the density at 0° C. and 760 mm. (the molecular volume) approximates very closely the value 22·412 for an ideal gas, but in the case of carbon dioxide the value becomes 22·268. He therefore concludes that Avogadro's theory does not hold in this case.

Haber ("Thermodynamics of Technical Gas Reactions," 1906, p. 306) does not consider Wohl's conclusions valid. He demonstrates his objections as follows:—

From Van der Waals's equation, the ratio between the pressure P, the volume V, and the temperature T of a gas is expressed thus:—

$$\left(P+\frac{a}{V^2}\right)(V-b) = RT.$$

Further, if d = density at 0° C. and 760 mm. pressure, and M the molecular weight, the following equation is derived:—

$$\frac{M}{d} = (1+a)(1-b) = R.$$

For carbon dioxide Van der Waals gives the following values:—

$$a = 0{\cdot}00874 \qquad b = 0{\cdot}00230$$

Therefore—

$$\left(\frac{M}{d}\right)1{\cdot}00646 = R = 22{\cdot}412.$$

The value $\frac{M}{d} = 22{\cdot}268$ = volume of a grm. molecule, then—

$$\frac{22{\cdot}268}{22{\cdot}412} = \frac{\text{molecular volume of carbon dioxide}}{\text{molecular volume of oxygen}},$$

This value is the same as that obtained by dividing the theoretical specific gravity by the observed specific gravity.

Haber therefore concludes that the deviation in the case of carbon dioxide is due only to the fact that at 0° C. and 760 mm. pressure carbon dioxide is not a perfect gas, and that the deviation has nothing to do with Avogadro's theory. Haber further shows from Van der Waals's equation that when V is large the term $\frac{a}{V^2}$ is negligible, and that the difference between V and $(V-b)$ is also negligibly small. The equation then becomes—

$$PV = RT = C.$$

Hence, as the partial pressure of a gas decreases from one atmosphere, the gas will more nearly behave like an ideal gas, or, in other words, there can be obtained some partial pressure at and below which the behaviour of the gas will differ so slightly from that of an ideal gas that the deviation will be negligible in eudiometry. This partial pressure can be obtained by diluting the gas whose behaviour deviates from that of an ideal gas with one, or a mixture of two or more gases, whose behaviour at 0° and 760 mm. pressure is sufficiently close to that of a perfect gas. Air, the chief constituents of which are oxygen and nitrogen, can be used.

In view of these facts Haber concludes that in order to avoid the use of corrected equations in calculating the percentages of combustible gases from the combustion data afforded by a gas analysis, such a small quantity of the combustible gas should be taken for the analysis that the carbon dioxide produced by the combustion does not exceed 30 per cent of the total quantity of gas measured; that is, its partial pressure should not exceed 30 per cent of the total pressure after combustion.

Authors' Comments on Work of Wohl and Haber.

In summing up the work of Wohl and Haber regarding the true molecular volume of gases the authors of this paper comment as follows:—

1. In exact gas analysis by slow combustion, Wohl's observation that the combustion data must be corrected when the partial pressure of the carbon dioxide produced is high has been confirmed.

* *Technical Paper* 54, Department of the Interior, U.S.A. Bureau of Mines.

2. The authors agree with Haber that Wohl's expressions can be used only in special cases when the partial pressure of the carbon dioxide constitutes nearly 100 per cent of the total pressure.

3. The authors disagree with Haber's conclusion that the best method of making combustion analyses is to keep the partial pressure of the carbon dioxide so low (less than 30 per cent of the total pressure) in the gases measured after the combustion as to eliminate the use of corrected equations. Their conclusion is reached by reasoning as follows:—

Sources of Error in Gas Analyses.

In the analyses of some mixtures rich in combustible gases so small a proportion of the original gas has to be used in order to keep the partial pressure of the CO_2 produced below 30 per cent that a small error of manipulation is magnified many times when the calculation to a percentage basis is made. In many forms of gas analysis apparatus such errors are unavoidable, and even in the use of apparatus designed for exact work they occur to some extent.

The point is illustrated by the following data relating to an analysis of natural gas by the explosion method (Table I.). For the analysis only a small proportion of the sample was taken.

TABLE I.—*Analysis of a Sample of Natural Gas by the Explosion Method.*

	Cc.
Volume of sample taken	7·0
Volume after carbon dioxide absorption	7·0
Air added	93·0
Total volume	100·0
Volume after explosion	85·5
Contraction	14·5
Volume after absorption of carbon dioxide	77·3
Carbon dioxide produced	8·2

If x = partial methane
and y = partial ethane,
then $2x+2\cdot5y = 14\cdot5$,
$x+2y = 8\cdot2$.
From which $x = 5\cdot68$,
$y = 1\cdot26$,
$CH_4 = 81\cdot1$ per cent,
$C_2H_6 = 18\cdot0$ per cent.
Total paraffins = 99·1 per cent.

If one makes an error of, say, $+0\cdot1$ cc. in reading the volume after explosion and an error of $-0\cdot1$ cc. in reading the carbon dioxide absorption, the figures become:—

$$2x+2\cdot5y = 14\cdot4$$
$$x+2\cdot0y = 8\cdot4$$
$$x = 5\cdot2$$
$$y = 1\cdot6$$
Percentage of CH_4 = 74·3
Percentage of C_2H_6 = 22·8

Percentage of total paraffins = 97·10, or a difference of 2 per cent.

The results of an analysis of a sample of methane by the explosion method are also illustrative (Table II.).

TABLE II.—*Analysis of a Sample of Pure Methane.*

	Cc.
Volume of sample taken	8·0
Volume after carbon dioxide absorption	8·0
Air added	92·0
Total volume	100·0
Volume after explosion	84·0
Contraction	16·0
Volume after absorption of carbon dioxide	76·0
Carbon dioxide produced	8·0

If an error of $\pm0\cdot1$ cc. be made in reading the volume after the carbon dioxide absorption, then hydrogen, carbon monoxide, or some hydrocarbon other than methane is indicated. If instead of the carbon dioxide reading being 8, it was 7·9, then instead of the methane calculating to 100 per cent, it would calculate to only 98·7 per cent—a difference of 1·3 per cent. Therefore if one were examining a gas for its purity one could not be sure whether or not there was some other gas present, at least to the extent of 1 per cent.

In many cases, however, the partial pressure of the carbon dioxide can be kept low, the use of corrected equations being thus avoided. At the same time such a quantity of the sample can be used for analysis as not to increase the experimental error appreciably. For instance, the partial pressure of the carbon dioxide can be kept low in mixtures containing small proportions of methane, carbon monoxide, ethane, coal-gas, blast-furnace gas, or producer gas. But for mixtures in which the carbon gases constitute almost the whole of the sample it is much better to use the slow combustion method, taking such a quantity of the sample that the oxygen added for combustion will be only a few cc. in excess of that theoretically required, and applying corrected equations.

(To be continued).

THE SCIENTIFIC WEEK.

(From Our Own Paris Correspondent).

THE SOLAR STORMS.

The magnetic storms of the sun that cause the magnet needle to vibrate at a distance of more than 150,000 kilometres, and which disturb the telephonic communication of our planet, are, as we are aware, particular phenomena of the solar activity. These storms take place in the spots of the sun, which spots are regulated by a general law, the cause of which is not yet discovered, but which makes them increase and decrease periodically, following a rhythm of about eleven years. The origin of these spots remains, however, still mysterious. Very recent researches by Dr. J. A. Harker, of the National Physical Laboratory, will very probably somewhat elucidate these obscure phenomena. This learned man has studied the electrical emissivity of matter, and he has noticed that this said emissivity is intimately related to the problem of incandescent lighting. Mr. Harker recalls to mind the fact that the conductibility of bodies is only a question of temperature. At very high temperatures all bodies are conductors, and this is so true that in those conditions no good isolators are known. Some years ago Guthrie had observed that an iron sphere charged with electricity loses its charge at a red-heat, if it is electrified positively, and also at a white-heat whatever may be the nature of its electricity. The phenomenon of emissivity of matter was studied for the first time by Elster and Geitel, then by Richardson. All these *savants* have remarked that metals and carbon at high temperatures emit electrified particles. At somewhat lower temperatures, during the expulsion of the impurities and the gases of the metals, the particles are positive. At very high temperatures these particles are negative. But the emission of particles negatively electrified is much more considerable than the emission of positive particles. This law seems to be general. All heated metals emit electricity in the form of currents. Very recent observations of two American astronomers, Messrs. Hale and King, of the Mount Wilson Observatory, have shown that powerful magnetic fields exist in the sun; this seem necessary for the explanation of certain phenomena of the sun's spots, as the result of the emission of swarms of electrical charged particles. The formidable magnetic whirlwinds, the powerful electrical discharges which take place in the sun, and which give birth to the Hertzian waves, and the cathodic rays emitted by the sun, have no other cause than the fusion of the metals in the solar furnace.

THE VARRON OF THE OX.

A new and important communication has just been made to the Academy of Sciences by M. Edmond Perrier, Director of the Natural History Museum, in the name of M. Adrien Lucet, Member of the Academy of Medicine, concerning the hypoderm fly or *varron* of the ox. The larvæ of these flies secrete under the skin of the back of the ox, where they increase in size and cause abscesses. The animals attacked in this way grow thin and the flesh is unserviceable, and their hides become pierced like a sieve. For these reasons agriculture and the leather industry lose enormous sums annually. In order to extract the larvæ the only means known up till now was to press the abscesses enclosing them with the hands, or else, after having opened the tumour, to take them out with the help of pincers. According to numerous experiments he has performed, M. Lucet affirms that it is possible to destroy this parasite in the bovine species in the sub dermic tumours where they live by the aid of the injection into these tumours of a few drops of tincture of iodine.

THE MINERVITES.

The minervites are double phosphates of alumina and alkali that M. Armand Gautier discovered in 1892 in the grottoes of Minerva in the Herault Department. Since then they have been met with in diverse places, in the Island of the Reunion, in the province of Oran, &c., but always in grottoes where primitively had become accumulated animal deposits and excrements, transformed first into guano, then into alkaline phosphates that have attacked the aluminous outer rock. These minervites are white substances, or else slightly tinted with yellow resembling kaolin, but containing 40 per cent of phosphoric acid and as much as 15 and 16 per cent of potash. It is easy to understand what a treasure and richness they would represent for agriculture if continuous banks of minervites were discovered. In the grotto of Minerva they are found in contact with the Permian red sandstone rocks in stratifications discordant with the nummulitic. They there fill kinds of pockets to which is superposed a thick layer of earthy and clayey phosphates, amongst which are scattered very large quantities of the bones of the cave bears, of rhinoceros, of hyænas, of small gnawing animals, of bats, &c. The deposit discovered in 1892 by M. Armand Gautier represents not less than 100,000 tons of phosphated manure.

AN ELEGANT METHOD FOR DETERMINING THE DIFFERENCES OF LONGITUDE.

Prof. Lippmann has just discovered an exceedingly ingenious photographic method which enables the measuring of the difference of longitude existing between two localities. This method consists in taking simultaneously at each of the two stations a photograph of the sky, placing at the zenith an artificial star. By reducing these two photographs in the same way as is done for the photographic map of the sky, it is easy to calculate the difference of longitude to about a fraction of a second of an arc or segment, that is to say, with an uncertainty of merely scarcely 3 or 4 metres.

THE RÔLE OF LICE AND THEIR DESCENDANTS IN THE TRANSMISSION OF INFECTIOUS DISEASES.

Dr. Roux, of the Pasteur Institute, has presented to the Academy of Sciences a paper of MM. Sergent, Folley, and Viola on the experimental transmission to men and monkeys by the intermediary of the louse, not only of intermittent fever, but of exanthematic typhus and probably of various other affections. The microbe of typhus is hereditary in the descendants of the louse; that is to say, that the egg, the larva, and the parasite itself are infected from generation to generation. This is the first time that this has been remarked, and naturally it vastly increases horror of these detestable little insects.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, April 2, 1914.

SIR WILLIAM CROOKES, O.M., President, in the Chair.

THE Bakerian Lecture was delivered by Prof A. FOWLER, F.R.S.

Series Lines in Spark Spectra.

This investigation was undertaken in continuation of that on the new lines (λ 4686, &c.) produced in 1912 by passing strong discharges through helium tubes containing an impurity of hydrogen. These lines are of great interest in celestial spectroscopy, and, following Rydberg, they were at first attributed to hydrogen. They have since become of increased importance, in connection with theories of the constitution of the atom, through the theoretical work of Dr. Bohr, who explains them as being produced during the first stages in the reformation of helium atoms from which both electrons have been removed by the strong discharges employed.

Certain peculiarities of the "4686" series suggested a search for other series of similar character, in order that some generalisation with regard to them might be reached. Further experiments on magnesium have yielded many new enhanced (spark) lines, and valuable data for calcium, strontium, and barium have been provided by the work of other observers. The chief results may be summarised as follows:—

1. Enhanced (spark) lines form series which occur in groups similar to those previously recognised in arc spectra. The formulæ representing enhanced lines, however, differ from those employed for arc lines in that Rydberg's constant "N" (= 109,675 for Rowland's scale) has a value equal to 4N.

2. The fundamental series, in the case of enhanced lines, derives its limit, and the separation of its components, from an observed negative term of the diffuse series. The well known spark line of magnesium, λ 4481, is the first member of such a fundamental series in association with a newly-discovered system of doublets.

3. No numerical relations have been traced between any of the enhanced line series and the series of arc lines of the same elements.

4. The "4686" series produced in helium tubes is of the enhanced line (4N) type, and can no longer be considered to belong to the same group as the Balmer series of hydrogen lines, which is of the arc (N) type. The "4686" series and the associated "Pickering" lines, as indicated by Bohr, are in all probability due to helium, and should be designated "proto helium" lines in accordance with the nomenclature of Lockyer.

5. Analogy with the "4481" series of magnesium suggests that the "4686" series of proto-helium is primarily of the fundamental type, while the three associated series may be considered to be coincident with it. The Pickering lines are represented in magnesium by a combination series which is derived from the fundamental.

6. Bohr's theoretical formulæ for hydrogen and helium are in close accordance with the facts of observation. Adopting these formulæ, the spectroscopic data at present available give the mass of the hydrogen atom in terms of the mass of the electron as 1836 ± 12.

SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

Ordinary Meeting, April 1, 1914.

Mr. A. CHASTON CHAPMAN, President, in the Chair.

MESSRS. Robert Bickerstaffe, Thomas Henry Byrom, Sydney George Clifford, Donald Richard Frazer, and John McLaren were elected Members of the Society.

Certificates were read for the second time in favour of Messrs. Lauchlan Henry Dyke Acland, Frederic Herbert Lees, William Henry Woodcock, and Walter Alan Gibbings.

The following papers were read:—

"*The Water of Dorton Spa.*" By C. AINSWORTH MITCHELL.

Dorton: A forgotten Spa. Brief outline of history. A remarkable water. Iron (46 parts per 100,000) present as basic sulphate. Analyses by Prof. Brand (circ. 1830). Present composition of the water.

"*On Damage caused to Vegetation by Sulphurous and Sulphuric Acid in the Atmosphere.*" By R. R. TATLOCK and R. T. THOMSON.

The mere fact of the presence of sulphates in plants in excess of the proportion found in vegetation grown in a pure atmosphere is no proof of damage by sulphur acids. This is shown by results of analysis of plants from various localities, and the authors conclude that such damage can only be proved if (1) the percentage of SO_3 is considerably above that present in the plant normally, and (2) the leaf or other part of the plant, when moistened on the surface with water, gives an acid reaction with litmus, phenolphthalein not being admissible.

"*The Abnormal Refraction of Milk Serum.*" By J. McCRAE.

The author gives some results he has obtained during the analysis of certain abnormal but genuine milks produced in the Transvaal. The milk serum obtained from the samples, when examined by the Zeiss Immersion Refractometers at 20° C. gave results as low as 32·3. The normal minimum refraction of milk serum has been previously shown by the author to be 36 when, as in the present cases, the reagent employed for coagulation is sulphate of copper.

The cattle were apparently in good condition and the veldt grass was plentiful.

NOTICES OF BOOKS.

Photo-Chemistry. By S. E. SHEPPARD, D.Sc. (Lond.). London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1914.

THE establishment of photo-chemistry as an independent branch of science may now be regarded as definitely accomplished, and this text-book will probably be for some time used as a standard work on the subject. It has many merits, prominent among them being its completeness and the fullness of its bibliographical references. The measurement of light quantities is first discussed, with short descriptions of the apparatus employed for the purpose, and the classification of light sources according to their economic and energetic relations is well treated. The statics and dynamics of photo-chemical change and the consideration of light as the resultant of chemical change are subjects which are discussed in great detail, and a chapter is devoted to organic photosynthesis, with special reference to the building up of food stuffs by chlorophyll. It is occcasionally not easy to arrive at the author's exact meaning, and his style is sometimes decidedly involved. The book, however, is obviously intended chiefly for the expert and the advanced student, who will no doubt be able successfully to interpret the rather unusual phraseology.

Über die Konstitution und Konfiguration von Verbindungen höherer Ordnung. ("On the Constitution and Configuration of Compounds of higher Order"). By Prof. Dr. ALFRED WERNER. Berlin: Julius Springer. 1914.

IN this lecture, which was delivered at Stockholm in 1913, Prof. Werner gave a résumé of his hypothesis concerning the arrangement of atoms in molecules. The structure and space formulæ of the molecular compounds of cobalt, chromium, and platinum were briefly discussed, and a short account was given of the theory of principal and auxiliary valencies. The lecture gave an excellent sketch of Prof. Werner's views and of the work which has been done by himself and by other investigators in confirmation of them.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clviii., No. 8, February 23, 1914.

Preparation of Benzhydrol and of Symmetrical Tetraphenylethane.—Paul Sabatier and M. Murat.—To prepare benzhydrol either benzoic aldehyde or ethyl formate is allowed to act on phenyl magnesium bromide. The crystalline mass is treated with water acidified with sulphuric acid, the solution is saturated with sodium bicarbonate, the ethereal liquid decanted off, and the ether driven off by heating on the water-bath. On cooling crystals of nearly pure benzhydrol are deposited. If instead of driving off the ether the liquid is directly distilled, the chief product is symmetrical tetraphenyl ethane. When impure benzhydrol is distilled it rapidly decomposes owing to the catalysing action of the impurities, and this fact accounts for the formation of symmetrical tetraphenyl ethane. Pure fused benzhydrol, on the other hand, can be distilled at 298° under the ordinary pressure without undergoing any appreciable decomposition.

Verification of Laws of Transparence of Matter towards X-Rays.—Louis Benoist and Hippolyte Copaux.—The laws of transparence of matter towards X-rays show that transparence is essentially an atomic property. If the mass is equal per unit of surface exposed, and the quality of the rays is the same, the elements are less transparent the higher their atomic weights. The masses of equal transparence (equivalents of transparence) generally decrease as the atomic weights increase, and are represented by a well-defined curve. The authors have calculated the equivalents of transparence of three minerals, potassium ferrocyanide, cobaltic chloropentamine, and potassium silico molybdate, and have compared the results with the values obtained experimentally. The agreement between the two sets of numbers is very good, and thus the laws of transparence are confirmed.

Influence of Ethylenic Bond and of Carbonyl and Carboxyl Groups on the Absorption of Ultra-violet Rays.—Jean Bielecki and Victor Henri.—The characteristic band of carbonyl is influenced by the presence of a carboxyl or an ethylene bond in the molecule. In general, when a molecule contains two chromophores they mutually influence one another; if they are not too close in the molecule the result is an exaltation of the absorption—a hyperchromic effect. If the two chromophores are close together in the conjugate position there is more displacement of the characteristic bands of each chromophore towards the red, a hypsochromic effect.

Decomposition of Ammonia under the Action of Radium Emanation and Influence of Temperature upon Chemical Effects produced by Radiations of Radio-active Substances.—Eugène Wourtzel.—Ammonia is decomposed by radium emanation into nitrogen and hydrogen, and no other reaction takes place. The quantity of gas evolved per unit of radiation destroyed increases with the pressure, but tends towards a certain limit. An increase of temperature favours the destruction of ammonia. Thus the number of cubic centimetres of ammonia destroyed per unit of radiation is nearly double at 108° and more than triple at 220°.

Bromination of Manganese in Ethereal Medium.—F. Ducelliez and A. Raynaud.—If bromine is added to

ether containing metallic manganese the ether which is first coloured red is gradually decolorised, and a semi-fluid orange deposit is formed. In presence of sulphuric acid this substance loses ether and forms crystals of formula $MnBr_2(C_2H_5)_2O$. When it is heated it yields white anhydrous $MnBr_2$. If the quantity of bromine in the original operation is greatly increased the deposit formed has the composition represented by the formula $MnBr_3(C_4H_{10}O)_3$.

Preparation of Pure Metals.—Maurice Billy.—Refractory metals such as titanium can be prepared by reducing their chlorides with hydrogen or sodium. In the former case a very high temperature is necessary, and it difficult to prevent oxidation if sodium is used. Both of these difficulties are avoided by the employment of sodium hydride. The reduction of the chlorides is complete at about 400°, the equation being $TiCl_4+NaH=Ti+4NaCl+4H$. Vanadium tetrachloride can be reduced similarly. It is necessary to dry the metal in a current of CO_2, for it catches fire in air spontaneously at 100°.

Etherification of Glycerin by Acetic Acid in Presence of Catalysts.—J. B. Senderens and Jean Aboulenc.—Potassium bisulphate acts catalytically in the etherification of glycerin by acetic acid, and anhydrous aluminium sulphate has a similar but stronger action. The results are still better when sulphuric acid is used as catalyst.

MISCELLANEOUS.

Royal Institution.—On Tuesday next, April 21, at 3 o'clock, Dr. Walter Wahl will deliver the first of two lectures at the Royal Institution on "Problems of Physical Chemistry—(1) Study of Matter at High Pressures; (2) Study of Matter at Low Temperatures"; on Thursday, April 30, Dean Inge will begin a course of three lectures on "The Last Chapter of Greek Philosophy—Plotinus as Philosopher, Religious Teacher, and Mystic"; and on Saturday, April 25, Dr. T. E. Stanton commences a course of two lectures on "Similarity of Motion in Fluids—(1) The Theory of Similarity of Motion in Fluids and the Experimental Proof of its Existence; (2) The General Law of Surface Friction in Fluid Motion." The Friday Evening Discourse on April 24 will be delivered by Dr. Frank Watson Dyson (the Astronomer Royal) on "The Stars Around the North Pole," and on May 1 by Mr. E. F. Benson on "A Criticism on Critics."

The Institute of Metals.—*May Lecture.*—Prof. E. Heyn, of Berlin, one of the most famous scientists in Germany, is this year to deliver the annual May Lecture before the Institute of Metals. Prof. Heyn, who has made a life-long study of the subject, has given the title of his discourse as "Internal Strains in Cold Wrought Metals, and some Troubles Caused Thereby." The Institute of Metals is fortunate in its May lecturers, and in the natural sequence of the subjects dealt with at these lectures. Thus, the last May Lecture, by Sir J. Alfred Ewing, K.C.B., F.R.S., was on the subject of "The Inner Structure of Simple Metals," and previously Dr. G. T. Beilby, F.R.S., had lectured on an allied subject, "The Hard and Soft States in Metals." Prof. Heyn's discourse will be given in the building of the Institution of Mechanical Engineers, Storey's Gate, Westminster, S.W., under the Chairmanship of Admiral Sir Henry Oram, K.C.B., F.R.S., the President of the Institute of Metals, on Tuesday, May 12, at 8.30 p.m. The Secretary of the Institute, Mr. G. Shaw Scott, M.Sc., of Caxton House, Westminster, S.W., will be glad to forward tickets to any readers who may desire to be present at the May Lecture.

Iron and Steel Institute.—The Annual Meeting of the Institute will be held in the new House of the Institution of Civil Engineers, Great George Street, Westminster, on Thursday and Friday, May 7 and 8, 1914, commencing each day at 10.30 o'clock a.m.

Programme of Proceedings.

Thursday, May 7, at 10.30 a.m., General Meeting of Members; the Council will present their Report for the year 1913; the Hon. Treasurer will present the Statement of Accounts for 1913; Scrutineers will be appointed for the examination of voting papers for election of new Members of the Institute; the retiring President (Mr. Arthur Cooper) will induct into the Chair the President-elect (Mr. Adolphe Greiner); the Bessemer Gold Medal for 1914 will be presented to Mr. Edward Riley, F.I.C.; the President will deliver his Inaugural Address; a selection of papers will be read and discussed (Nos. 16, 10, 8); papers Nos. 5, 12, 15 will be read and discussed as far as time permits. At 7.0 p.m., Annual Dinner of the Institute at the Connaught Rooms, Great Queen Street, W.C.

Friday, May 8, at 10.30 a.m., General Meeting of Members; the Andrew Carnegie Gold Medal (for 1913) will be presented to Mr. Thomas Swinden, D.Met., and the award of Research Scholarships for the current year will be announced; papers Nos. 14, 9, 11 will be read and discussed; if time permits other papers may be discussed at any of the Sessions, in which case due notice will be given. Those papers for which time cannot be found will be taken as read and discussed by correspondence.

The following is the list of papers that are expected to be submitted for reading and discussion:—

1. J. O. Arnold, D.Met., F.R.S., and G. R. Bolsover: "Forms in which Sulphides may Exist in Steel Ingots."
2. C. Benedicks, Ph.D.: "Experiments on Allotropy of Iron (Behaviour of Ferromagnetic Mixtures; Dilatation of Pure Iron)."
3. A. Bose: "Recent Developments of the Iron and Steel Industry in India."
4. C. Chappell: "The Re-crystallisation of Deformed Iron."
5. C. A. Edwards, D.Sc., and H. C. H. Carpenter, Ph.D.: "The Hardening of Metals, with Special Reference to Iron and Its Alloys."
6. J. N. Friend, D.Sc., and C. W. Marshall: "Influence of Molybdenum upon the Corrodibility of Steel."
7. H. C. Greenwood, D.Sc.: "Note on a Curious Case of Decarburisation during the Hardening of Steel Dies."
8. Sir Robert A. Hadfield, F.R.S., and B. Hopkinson, F.R.S.: "The Magnetic and Mechanical Properties of Manganese Steels."
9. H. L. Heathcote, B.Sc.: "Some Improvements in Case-hardening Practice."
10. S. A. Houghton: "Failures of Heavy Boiler Shell Plates."
11. E. Humbert and A. Hethey, B.Sc.: "Production of Steel Direct from the Ore."
12. A. McCance, B.Sc.: "Theory of Hardening."
13. M. Misson: "The Colorimetric Estimation of Sulphur in Pig Iron and Steels by means of Paper Impregnated with a Solution of Arsenious Anhydride in Hydrochloric Acid."
14. F. Müller: "The Development of Dry Cleaning in Blast-furnace Gas Purification."
15. W. Rosenhain, D.Sc., F.R.S., and J. L. Haughton, M.Sc.: "A new Reagent for Etching Mild Steel."
16. F. Schuster, D.Ing.: "Results of Talbot Process at Witkowitz."

MEETINGS FOR THE WEEK.

Tuesday, 21st.—Royal Institution, 3. "Problems of Physical Chemistry," by W. Wahl, Ph.D.

Wednesday, 22nd.—Faraday Society, 8. "Recording Pyrometers," by C. R. Darling. "Embrittling of Iron by Caustic Soda," by J. H. Andrew. "Diffusion and Membrane Potentials," by E. B. R. Prideaux. "Acidic and Colloidal Properties of Aluminium Hydroxide," by R. E. Slade and W. G. Polack. "On Negative Adsorption," by A. M. Williams.

Friday, 24th.—Royal Institution, 9. "The Stars around the North Pole," by F. W. Dyson, F.R.S., &c.

Saturday, 25th.—Royal Institution, 3. "Similarity of Motion in Fluids," by T. E. Stanton, D.Sc., &c.

THE CHEMICAL NEWS

VOL. CIX., No. 2839.

A FURTHER EXPERIMENT ON THE COLOUR OF COBALT SALTS IN SOLUTION.

By J. E. MARSH.

WHEN a pink solution of cobalt and sodium chloride in a mixture of water and acetone is subjected to an electric current a blue layer collects at the anode. A solution containing 1 part by weight of sodium chloride, 2 of cobalt chloride $CoCl_2.6H_2O$, 8 of acetone, and 8 of water was placed in a U-tube. The town current of about 100 volts with lamp resistance was passed through by means of carbon terminals. The light blue layer collected at the anode, the rest of the solution retaining its pink colour. On reversing the current the blue layer was decolorised at what was now the cathode and another blue layer appeared in the other limb of the tube. The U-tube should be cooled externally, otherwise, owing to the heating effect of the current, the blue layer may appear temporarily in both limbs of the tube. The experiment illustrates very well the electro-negative character of the blue cobalt complex; the solution at the anode becomes supersaturated, with separation of the blue acetone layer. When a solution of cobalt chloride alone in water and acetone was treated in the same manner metallic cobalt separated at the cathode, and no separation into layers was observed.

UNUSUAL DOLOMITES

By NICHOLAS KNIGHT.

THE rock formation of North-east Iowa belongs to the Niagara period and is dolomitic in character. The various layers show slight differences, but on the whole they are typical dolomites, having the formula $CaCO_3,MgCO_3$. The analysis of a fair sample shows:—

	Per cent.
$CaCO_3$	54·35
$MgCO_3$	43·65
SiO_2	1·00
Fe_2O_3 and Al_2O_3	1·00
Total	100·00

About a year ago our attention was called to a peculiar dolomite from the Simplon Tunnel reported by Gabriele Lincio (*Reale Accademia delle Scienze di Torino*, 1911). On analysis the specimen was found to have the formula $3CaCO_3,2MgCO_3,FeCO_3$, and so is called a ferriferous dolomite.

At our suggestion Mr. C. B. Smith analysed specimens from a number of different layers of the dolomite rock in Mount Vernon, Iowa, and vicinity. He found a peculiar looking specimen at the "Palisades," on the Cedar River, about six miles from Mount Vernon. The specimen is coarse granular, pinkish to reddish brown, resembling iron rust, with white crystals disseminated through it. It is quite a deep red in certain portions. The specimen occurs in pockets in the regular dolomite rock. The analysis by Mr. Smith resulted as follows:—

	Per cent.
$CaCO_3$	64·50
$MgCO_3$	33·87
SiO_2	0·57
Fe_2O_3 and Al_2O_3	0·96
Tota	99·90

The analysis did not show the amount of iron that the appearance of the rock led us to expect. The figures correspond quite closely to the formula $3CaCO_3.2MgCO_3$, the iron alumina and silica replacing the equivalent amount of magnesium carbonate.

Other specimens from the same locality that seemed to differ in appearance from the typical layers resulted as follows:—

		Per cent.
(1)	$CaCO_3$	52·81
	$MgCO_3$	46·15
	SiO_2	0·37
	Fe_2O_3 and Al_2O_3	0·68
	Total	100·01
(2)	$CaCO_3$	51·52
	$MgCO_3$	47·06
	SiO_2	0·53
	Fe_2O_3 and Al_2O_3	0·58
	Total	100·01

The analyses show the small amounts of silica, iron, and alumina; these three constituents aggregate about 1 per cent.

Attention has been called to another iron-bearing dolomite from the Simplon Tunnel by Mario Delgrosso (*Riv. Min. Crist. Ital.*, xli., 56—64). This differs from all the foregoing specimens. The analysis leads to the formula $4CaCO_3,3MgCO_3,(Fe,Mn)CO_3$.

O. Kallauner (*Chem. Zeit.*, xxxvii., 1317) has studied the thermal dissociation of normal dolomite. He found that dissociation into the two constituents, $CaCO_3$ and $MgCO_3$, begins at 500° and reaches a maximum between 710° and 730°. At higher temperatures the $MgCO_3$ and $CaCO_3$ dissociate.

It might prove interesting and instructive to study the thermal dissociation of some of the abnormal specimens.

Cornell College, April 1, 1914.

SIMPLE AND COMPLEX ROTATORY DISPERSION.*

By T. MARTIN LOWRY and T. W. DICKSON.

THE object of the present paper is to discuss the form of the curves of rotatory dispersion in the light of experimental evidence obtained in a series of recent investigations. Some of these have already been published, whilst others are still awaiting completion. (Lowry, *Proc. Roy. Soc.*, 1908, A. lxxxi., 472; *Phil. Trans.*, 1912, A. ccxii., 261; *Trans. Chem. Soc.*, 1913, ciii., 1062. Lowry and Dickson, *Ibid.* 1067. Lowry, *Ibid.* 1322; *Trans. Chem. Soc.*, 1914, cv., 81. Lowry, Pickard and Kenyon, *Ibid.* 94. Lowry and Dickson, *Proc. Chem. Soc.*, June 5, 1913).

The experiments cover all the different varieties of optical rotation, namely: (1) the natural rotations observed in crystals of quartz, and (2) the artificial rotatory power produced by placing it in a magnetic field, (3) and (4) the optical and magnetic rotation in optically-active liquids such as *sec*-butyl alcohol and its homologues. The experiments include observations in the ultra-violet and infra-red, as well as in the visible region of the spectrum.

A. *Rotatory Dispersion in Quartz.*

The only data which will permit a *rigid* test of the form of the curve of rotatory dispersion are those which have been obtained in the case of quartz. Whereas, in the case of other substances, it is very rarely practicable to obtain readings as large as 100°, it has been found possible

* A Contribution to a General Discussion on "Optical Rotatory Power," held before the Faraday Society, March 27, 1914

in the case of quartz to record an *observed* rotation exceeding 100,000°. In the visible region of the spectrum, readings can be taken to seven significant figures, with errors of observation amounting to only a few parts per million. The readings can be extended into the ultra-violet, at least as far as wave-length 2200 A.U., and at least as far as wave-length 20,000 A.U. in the infra-red. In the ultra-violet the readings can be taken without difficulty to 1°, and it would not be difficult, by mere perseverance, to reduce the errors of observation to about 0·1°. As the readings are larger than in the visible spectrum, the errors of observation are, relatively, not much greater; indeed, if attention be paid to the fact that the photographic observations are made on narrow spectrum-lines, whilst the visible readings are taken with wide blocks of light, the greater spectral purity of the ultra-violet readings may impart to them a higher degree of accuracy than that actually attained by visual observation. The infra-red readings are necessarily of a lower order of accuracy, but are of great value on account of the wide range of wave lengths which they cover.

The first formula for the rotatory dispersion of light in quartz was given by Biot, who suggested that—

$$\alpha = \frac{k}{\lambda^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The rotation produced in light of any colour being inversely proportional to the square of the wave-length. Boltzmann gave the equation—

$$\alpha = \frac{k_1}{\lambda_2} + \frac{k_2}{\lambda^4} + \frac{k_3}{\lambda^6} + \quad . \quad . \quad . \quad . \quad . \quad (2)$$

corresponding closely with the Cauchy formula for refractive indices. Drude ("Theory of Optics," 1917, p. 413) suggested a general equation—

$$\alpha = \Sigma \frac{k_n}{\lambda^2 - \lambda_n^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

this equation, if $\lambda > \lambda_n$, can be expanded into a series of the same type as Boltzmann's equation (2).

In Drude's equation the constants λ_n are the wave-lengths *in vacuo* of light having the same periods as the natural periods of free vibration of the "ions" or "electrons" by which the optical properties of the molecule are determined. In the case of quartz the values of these constants have been deduced from measurements of refractive power as follows—

$$\lambda_1^2 = 0{\cdot}010627\ \mu^2$$
$$\lambda_2^2 = 78{\cdot}22\ \mu^2$$
$$\lambda_3^2 = 430{\cdot}6\mu^2.$$

Drude assumed that these refraction-data could be used to determine the course of the curve of rotatory dispersion. He therefore wrote the equation in the form—

$$\alpha = \frac{k_1}{\lambda^2 - \lambda_1^2} + \frac{k_2}{\lambda^2 - \lambda_2^2} + \frac{k_3}{\lambda^2 - \lambda_3^2} + \frac{k'}{\lambda^2} \quad . \quad . \quad . \quad (4)$$

and calculated the values of k_1, k_2, k_3, &c., from existing data for the rotatory power of quartz over the range from 21,400 A.U. (2·140 μ) to 2193·5 A.U. (0·21935 μ). He found $k_2 = k_3 = 0$, and concluded (i.) "*that the kinds of ions whose natural periods lie in the ultra-red are inactive.*" On the other hand, he had already adopted the view that quartz has ions for which λ_n is much smaller than the wave-length of light, and concluded (ii.) "that the activity coefficient k' of ions of this kind, for which λ^2 may be neglected in comparison with λ_2, must be taken into consideration." By throwing the equation into the form—

$$\alpha = \frac{k_1}{\lambda^2 - \lambda_1^2} + \frac{k'}{\lambda^2} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where $\lambda_1^2 = 0{\cdot}010627$, $k_1 = 12{\cdot}200$, $k' = -5{\cdot}046$, Drude was able to calculate the rotatory power of quartz over the whole range with an average error of 0·060° per mm. in a series of 18 observations.

The more accurate measurements put forward in 1912 could not be represented, even in the narrow range of the visible spectrum, by Drude's simplified equation (5). In order to secure a reasonable concordance between the observed and calculated values, it was necessary to go back upon Drude's first conclusion and to restore an infra-red term to the equation, which thus became—

$$\alpha = \frac{k_1}{\lambda^2 - \lambda_1^2} + \frac{k_2}{\lambda - \lambda_2^2} + \frac{k'}{\lambda^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

This formula gave results which were a great improvement on the figures quoted by Drude, the average discrepancy in the visible region of the spectrum being reduced from 0·038 to 0·001° per mm.

Further measurements in the ultra-violet region, which are not yet available for publication, show that even this improved formula becomes grossly inaccurate when carried out towards the limit of transmission of light by quartz. It cannot be made to give good results so long as the values of λ_1^2 and λ_2^2 deduced from the refraction data are used as constants in the equation, thus limiting the number of arbitrary constants to three. The value of the infra-red term is not important, as it comes into the equation as a quantity that remains almost constant over a wide range of the spectrum; there is therefore no objection to retaining the value of λ_2^2 deduced from the refractive power of the crystal in the extreme infra-red. But there is good reason to think that the value of λ_1^2 has been given incorrectly, and that the value of this constant may be deduced with much greater accuracy from exact observations of rotatory dispersion than from measurements of refractive power.

It is impossible at present to state the final form of the equation, but a very satisfactory agreement can be obtained over the whole range from w.l. 16,740 to w.l. 2327 by using Drude's general equation with *three* terms, namely, one infra-red term and two ultra-violet terms, thus—

$$\alpha = \frac{k_0}{\lambda^2 - \lambda_0^2} + \frac{k_1}{\lambda^2 - \lambda_1^2} + \frac{k_2}{\lambda^2 - \lambda_2^2} \quad . \quad . \quad (7).$$

In this equation $\lambda_2^2 = 78{\cdot}22$ as before; λ_1^2 is a constant differing somewhat from the value 0·010627 given by Drude; λ_0^2 represents another wave length in a remote part of the inaccessible ultra-violet region. Its magnitude is not negligible as Drude supposed, but is so small that the "probable error" as determined from the incomplete data at present available was found to be larger than the number itself. An equally good agreement can, however, be reached by replacing the whole of the infra-red term by a constant, putting $\lambda_0^2 = 0$, and regarding λ_1^2 as an unknown quantity. The equation then becomes—

$$\alpha = \frac{k_0}{\lambda^2} + \frac{k_1}{\lambda_2 - \lambda_1^2} + k_2 \quad . \quad . \quad . \quad . \quad (8).$$

This equation contains four arbitrary constants, as compared with the three arbitrary constants of equation (6) and the five arbitrary constants of equation (7). This number of constants appears to be quite sufficient to express the data at present available, and, from the empirical point of view, affords the most satisfactory solution of the problem of reducing the data to algebraic form.

B. *Optical and Magnetic Rotatory Dispersion in Simple Organic Liquids.*

In the case of a large number of simple organic liquids, the optical and magnetic rotatory dispersion may be expressed by the equation—

$$\alpha = \frac{k}{\lambda^2 - \lambda_0^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9).$$

Thus the average values of the *magnetic* dispersion-ratios in a series of 25 substances have been found to compare with the calculated values as follows :—

	Li 6708.	Cd 6438.	Na 5893.	Hg 5461.	Cd 5086.	Cd 4800.	Hg 4359.
Obs.	0·647	0·705	0·850	1·000	1·164	1·321	1·636
Calc.	0·647	0·705	0·850	1·000	1·166	1·322	1·636

In the case of the *optical* rotatory power of phenylmethylcarbinol, $C_6H_5.CH(OH).CH_3$, the figures are:—

Obs.	0·629	0·687	0·839	1·000	1·184	1·361	1·736
Calc.	0·627	0·686	0·839	1·000	1·183	1·362	1·735

These figures show that the simple formula is sufficient to express the course of the curves of optical and magnetic rotatory dispersion within the limits of the visible spectrum.*

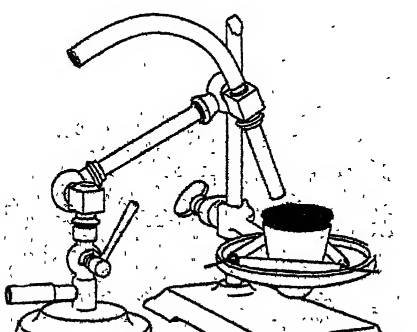
This does not prove that the substances in question are characterised by only one natural period of free vibration. Even in the case of quartz, which is known to possess four such natural periods, the optical rotatory power can be represented *within the same limits of accuracy* by the simple formula. But, until the methods of measurements have been developed to an extent which is now quite impracticable, the simple formula will hold its own, as the only possible way of expressing the experimental data in the case of simple organic liquids.

(To be continued).

THE PURIFICATION OF BARIUM SULPHATE PRECIPITATED IN THE DETERMINATION OF BARIUM.

By F. A. GOOCH and D. U. HILL.

WHEN in the determination of barium as the sulphate the precipitation is made in the presence of alkali salts, considerable errors—sometimes as much as 20 mgrms. in one half grm. of precipitate—may be occasioned by occlusion of the foreign salts. It has been found that upon dissolving the precipitate of barium sulphate in concentrated sulphuric acid and evaporating to dryness, the barium sulphate crystallises in more or less coarsely granular crystals which may be washed free from the other sul-



phates (Mar, *Am. Journ. Sci.*, 1891, xli., 295). The evaporation must be made with special care in order to avoid loss by spattering and creeping. With a ring burner this process takes several hours, but with a Hempel burner an evaporation can be made safely in about one half-hour. The present object has been to find out whether the evaporation cannot be safely made by directing the flame of a blast lamp down upon the surface of the liquid, thus substituting for the Hempel burner a piece of apparatus that is in more general use.

Preliminary experiments to determine whether an evaporation without loss of barium sulphate could be made with the blast lamp were carried out in the following manner:—Crystallised barium chloride (chemically pure) was powdered and bottled without drying, and the water content determined by gentle ignition. Of this salt portions of 0·5000 grm. each were weighed into a previously weighed platinum crucible. About 5 cc. of water was added, and then from 2 cc. to 5 cc. of sulphuric acid. The water and excess of sulphuric acid were evaporated off by directing a small flame from the blast lamp nearly vertically downward upon the liquid. The evaporation required about fifteen minutes. The results obtained upon weighing the crucible and barium sulphate were satisfactory in three cases out of five, but in the other two cases there was loss. To prevent this a cone of fine platinum gauze was fitted into the mouth of the crucible and the flame was directed against the point of the cone. This prevented the loss by spattering. The point of the cone must not be allowed to dip into the liquid, for otherwise some of the barium sulphate will be left above the gauze and may be blown away. The gauze was weighed with the crucible and cover each time, so that if any of the barium sulphate should spatter against the gauze its weight would not be lost. The results where the gauze was used were more consistently satisfactory, and we felt encouraged to carry on further experiments using the gauze, but not without it. The average time required for completing an evaporation in these and subsequent experiments where the gauze was used was about one half-hour. Table I. gives the results of the experiments in which the naked flame was directed upon the solution, Table II. those of the experiments in which the gauze was interposed.

TABLE I.

Wt. of $BaCl_2.2H_2O$ taken.	$BaSO_4$ found.	$BaSO_4$ by theory.	Error.
Grm.	Grm.	Grm.	Grm.
0·4996	0·4744	0·4773	+0·0001
0·4996	0·4774	0·4773	+0·0001
0·4996	0·4747	0·4773	−0·0026
0·4996	0·4773	0·4773	0·0000
0·4996	0·4765	0·4773	−0·0008

TABLE II.

0·4996	0·4770	0·4773	−0·0003 (*a*)
0·4996	0·4777	0·4773	+0·0004
0·4996	0·4768	0·4773	−0·0005
0·4996	0·4768	0·4773	−0·0005
0·4996	0·4774	0·4773	+0·0001
0·4996	0·4776	0·4773	+0·0003

(*a*) The tip of the gauze dipped into the liquid.

For use in the subsequent experiments a solution to contain approximately 0·5 grm. of $BaCl_2.2H_2O$ in 50 cc. was prepared by weighing out 20 grms. of the $BaCl_2.2H_2O$, transferring it to a 2-litre measuring flask, and filling the flask to the mark with distilled water. The quantity of the solution used in each experiment was determined by drawing portions of 50 cc. from a burette into previously weighed glass-stoppered Erlenmeyer flasks and weighing. Since 0·01 grm. of the solution contained only 0·0001 grm. of $BaCl_2.2H_2O$, it was not necessary to weigh more accurately than to 1 centigrm. However, the weighing was usually made to a milligrm.

In the first series of experiments determinations of barium in the absence of salts of other metals were made in the usual manner, and the effect of the treatment of the precipitate of barium sulphate with sulphuric acid in the way described was tried. The procedure in detail was as follows:—One cubic centimetre of strong sulphuric acid was added to 100 cc. of water in a 250 or 350 cc. beaker, and the mixture was heated to boiling. The weighed amount of barium chloride solution was washed from the

* Additional evidence in reference to the optical rotatory power of α-methylglucoside is given in another paper (Lowry and Abram, p. 171).

Erlenmeyer flask into the hot acid solution. The beaker was then allowed to stand on the steam-bath for a few hours, and in most cases at least one night intervened between the precipitating and the filtering of the material. The precipitate was filtered on ashless paper (ash 0·00011 grm.) without using pressure, ignited with the paper in a weighed platinum crucible, and brought to constant weight with a Bunsen burner. From 2 to 5 cc. of sulphuric acid were then added, the gauze cone fitted in the crucible, the evaporation made as in the previously described experiments, and the crucible with its contents, the gauze, and cover, weighed. Only a trifling change of weight would be expected, since the only solid material that could be occluded in the original precipitate is barium chloride. As this would take the place of an equivalent amount of the sulphate, and the molecular weights of the chloride and sulphate do not differ greatly, no very great error could be introduced in this way. In the reverse process—the determination of sulphate by precipitation with excess of barium chloride—"the occlusion of barium chloride in the precipitate of barium sulphate may lead to very serious error" (Richards and Parker, *Proc. Am. Acad. Sci.*, xxxi., 76). Table III. gives the results of the experiments just described, corrected for the filter-ash, 0·0001 grm.

In the next series of experiments, 10 cc. portions of a 20 per cent solution of potassium chloride were added to the 100 cc. of water and the 1 cc. of sulphuric acid before the precipitation was made. The procedure just described was then followed to the point where the evaporation with sulphuric acid was completed. The material was then washed from the crucible on to a filter-paper and washed thoroughly to remove the potassium sulphate. The filter was dried and ignited in the crucible, and the crucible and contents brought to constant weight. Table IV. gives the results of this series. Correction has been made for the weight of the ash (0·0001 grm.) of the second filter-paper, that of the first paper having been dissolved presumably by the treatment with sulphuric acid.

TABLE III.

Weight of $BaCl_2$ solution used.	$BaSO_4$ found. Before treatment.	After treatment.	Results reduced to 50 grms. of solution. $BaSO_4$ before treatment.	$BaSO_4$ after treatment.	$BaSO_4$ by theory.	Error.
Grm.	Grm.	Grm.	Grm.	Grm.	Grm.	Grm.
50·281	0·4767	0·4766	0·4740	0·4739	0·4737	+0·0002
50·348	0·4784	0·4771	0·4751	0·4738	0·4737	+0·0001
50·199	0·4764	0·4754	0·4745	0·4735	0·4737	−0·0002
50·293	0·4786	0·4165	0·4758	0·4737	0·4737	0·0000

TABLE IV.

50·262	0·4814	0·4749	0·4789	0·4724	0·4737	−0·0013
50·171	0·4870	0·4772	0·4854	0·4756	0·4737	+0·0019
50·281	0·4804	0·4759	0·4777	0·4732	0·4737	−0·0005
50·285	0·4838	0·4762	0·4810	0·4735	0·4737	−0·0002
50·330	0·4805	0·4755	0·4774	0·4724	0·4737	−0·0013
50·320	0·4818	0·4766	0·4787	0·4736	0·5737	−0·0001
50·278	0·4813	0·4765	0·4786	0·4738	0·4737	+0·0001
50·301	0·4804	0·4751	0·4775	0·4723	0·4737	−0·0014*
50·274	0·4797	0·4762	0·4771	0·4736	0·4737	−0·0001
50·235	0·4790	0·4753	0·4768	0·4731	0·4737	−0·0006
Average..	..		0·4789	0·4733		

* A slight loss by creeping was expected in this experiment.

This investigation shows that the evaporation can be carried out successfully with the use of the blast lamp and platinum gauze as a substitute for the Hempel burner, and that, although the accuracy of the results is not as great as could be wished, yet, where alkali salts are present, this method of purification reduces the otherwise very large error to a value at most not more than 1 or 2 mgrms. for half-a-grm. of barium sulphate.—*American Journal of Science*, xxxv., p. 311.

ERRORS IN GAS ANALYSIS DUE TO ASSUMING THAT THE MOLECULAR VOLUMES OF ALL GASES ARE ALIKE.*

By GEORGE A. BURRELL and FRANK M. SEIBERT.

(Concluded from p. 189).

Recent Specific Gravity and Molecular Volume Determinations.

RECENT specific gravity determinations (at 0° C. and 760 mm. pressure) for different gases and of the molecular volumes of carbon dioxide and ethane at various partial pressures are presented in Table III. (H. Landolt and R. Börnstein, "Physikalisch-Chemische Tabellen," 1912, p. 148).

TABLE III.—*Results of Specific Gravity Determinations of Various Gases.*

Gas.	Molecular weight.	Specific gravity (Air=1). Theoretical.	Observed.	Observer.	Theoretical / Observed.
CH_4	16·03	0·5538	0·5545	Baumé and Perrot	0·999
C_2H_6	30·05	1·0381	1·0494	Baumé and Perrot	0·990
CO	28·00	0·9673	0·9670	Leduc	1·000
CO	28·00	0·9673	0·9672	Rayleigh	1·000
CO_2	44·00	1·5201	1·5287	Leduc	0·994
CO_2	44·00	1·5201	1·5291	Rayleigh	0·994
N_2	28·02	0·9680	0·9674	Rayleigh	1·001
N_2	28·02	0·9680	0·9672	Leduc	1·001
O_2	32·00	1·1055	1·1054	Rayleigh	1·000
O_2	32·00	1·1055	1·1052	Leduc	1·000
C_2H_4	28·03	0·9683	0·9852	Saussure	0·983
C_2H_2	26·02	0·8989	0·9056	Leduc	0·992

TABLE IV.—*Molecular Volumes of Carbon Dioxide at 20° C. and Various Partial Pressures.*

Pressure. Mm.	Molecular volume.	Percentage of total pressure.
100	0·999	13·1
200	0·999	26·3
300	0·998	39·5
400	0·997	52·6
500	0·997	65·8
600	0·996	78·9
700	0·995	91·9
760	0·995	100·0

In compiling the table of molecular volumes of carbon dioxide (Table IV.), advantage was taken of the work of Rayleigh and Chappuis (see Note) on the coefficient of expansion of carbon dioxide. The specific gravity of carbon dioxide as given by Rayleigh was determined at 0° C. and 760 mm. pressure. The value at 20° C. and 760 mm. pressure was determined from the coefficient of expansion of carbon dioxide between 0° C. and 20° C.

(NOTE.—Rayleigh, "On the Densities of Carbonic Oxide, Carbonic Anhydride, and Nitrous Oxide," *Proc. Roy. Soc.*, 1897, lxii., 204; "On the Compressibility of Gases between One Atmosphere and Half an Atmosphere of Pressure," *Trans. Roy. Soc.*, 1905, cciv., 360. P. Chappuis, *Bull. Inst. Poids et Mes.*, 1903, xiii., 190).

TABLE V.—*Molecular Volumes of Ethane at 0° C. and Various Partial Pressures.*

Pressure (mm.).	Molecular volume.
100	0·999
200	0·997
300	0·996
400	0·995
500	0·994
600	0·992
700	0·991
760	0·990

* *Technical Paper* 54, Department of the Interior, U.S.A. Bureau of Mines.

TABLE VI.—*Results of Analyses of Methane from Different Sources.*

	Mine gas. Laboratory No.—					Methane prepared by method of Gladstone and Tribe.			Natural gas. Laboratory No.—	
	1986.	2492.	2781.	2990.	2481.	Sample 1.	Sample 2.	Sample 3.	3150.	3149.
Volume of sample taken (cc.) ..	33·70	45·75	38·70	42·30	43·70	42·00	31·40	47·15	41·70	40·40
Volume after carbon dioxide absorption (cc.)	33·70	45·75	38·70	42·30	43·70	41·95	31·40	47·15	41·70	38·40
Portion taken (cc.)	33·70	45·75	38·70	42·30	43·70	41·95	31·40	47·15	41·70	38·40
Oxygen added (cc.)	95·65	70·10	68·05	51·10	46·90	99·10	71·25	99·45	87·40	80·00
Total volume (cc.)	129·35	115·85	106·75	93·40	90·60	141·05	102·65	146·60	129·10	118·40
Volume after burning (cc.) ..	65·80	58·95	83·20	67·20	56·80	59·50	40·85	53·85	60·05	56·05
Contraction (cc.)	63·55	56·90	23·55	26·20	33·80	81·55	61·80	92·75	69·05	62·35
Volume after absorption of carbon dioxide (cc.)	34·30	30·65	71·40	54·15	39·90	18·90	10·15	7·90	25·75	25·05
Carbon dioxide (cc.)	31·50	28·30	11·80	13·05	16·90	40·60	30·70	45·95	34·30	31·00
Carbon dioxide (percentage of total pressure)	47·9	47·9	14·2	19·4	29·7	68·2	75·1	85·3	57·1	55·3
Molecular volume of carbon dioxide corrected from—										
Table IV.	0·997	0·997	—	—	—	0·997	0·996	0·996	0·997	0·997
Theoretical equation, one-half contraction minus carbon dioxide (cc.) ..	0·28	0·15	−0·02	0·05	0·0	0·18	0·20	0·43	0·22	0·18
Corrected equation; correction times contraction minus correction times carbon dioxide (cc.) ..	0·12	0·01	—	—	—	−0·03	+0·02	0·15	+0·05	0·02
Methane from uncorrected contraction (per cent)	94·3	62·2	30·5	31·0	38·7	97·1	98·4	98·4	82·8	77·2
Methane from uncorrected carbon dioxide (per cent)	93·5	61·9	30·5	30·9	38·7	96·7	97·8	97·5	82·3	76·7
Difference (per cent)	0·80	0·30	0·0	0·10	0·0	0·4	0·6	0·9	0·5	0·5
Methane from corrected contraction (per cent)	94·1	62·0	—	—	—	96·90	98·2	98·2	82·60	77·0
Methane from corrected carbon dioxide (per cent)	93·8	62·0	—	—	—	97·0	98·2	97·9	82·5	77·0
Difference (per cent)	0·30	0·0	—	—	—	0·10	0·0	0·3	0·10	0·00

TABLE VII.—*Analyses of Carbon Monoxide Mixed with Air.*
(Prepared by the action of concentrated sulphuric acid on oxalic acid).

	Sample 1.	Sample 2.	Sample 3.	Sample 4.	Sample 5.
Volume of sample taken (cc.)	50·95	31·50	52·95	51·20	54·25
Oxygen added (cc.)	39·50	77·90	35·40	36·15	47·40
Total volume (cc.)	90·45	109·40	88·35	87·35	101·65
Volume after burning (cc.)	66·10	94·40	62·95	62·60	75·60
Contraction (cc.)	24·35	15·00	25·40	24·75	26·05
Volume after absorption of carbon dioxide (cc.)	17·80	64·40	12·75	13·85	23·90
Carbon dioxide (cc.)	48·30	30·00	50·20	48·75	51·70
Carbon dioxide (percentage of total pressure)	73·1	31·8	79·7	77·8	68·4
Molecular volume of carbon dioxide corrected from—					
Table IV.	0·997	—	0·996	0·996	0·997
Theoretical equation (two times contraction minus carbon dioxide)	0·40	0·00	0·60	0·75	0·40
Corrected equation (correction times contraction minus correction times carbon dioxide)	−0·04	0·00	−0·01	+0·15	−0·07
Carbon monoxide from uncorrected contraction (per cent)	95·6	95·2	95·9	96·7	96·0
Carbon monoxide from uncorrected carbon dioxide (per cent)	94·8	95·2	94·8	95·2	95·3
Difference (per cent)	0·8	0·0	1·1	1·5	0·7
Carbon monoxide from corrected contraction (per cent)	95·1	—	95·2	95·9	95·5
Carbon monoxide from corrected carbon dioxide (per cent)	95·0	—	95·2	95·6	95·6
Difference (per cent)	0·1	—	0·0	0·3	−0·1

The graph was plotted from two values determined experimentally, the value at 20° C. and 760 mm. pressure and that at 20° C. and 380 mm. pressure.

Table V. gives the molecular volumes of ethane at 0° C. and various partial pressures.

The coefficient of expansion of ethane between 0° C. and 20° C. has not been determined; consequently the same molecular volume was used at 20° C., the ordinary laboratory temperature, as was determined by Baumé and Perrot at 0° C. The resulting error can be disregarded without introducing any appreciable error in the analysis, judging from the case of the molecular volume of carbon dioxide which at 20° C. is only 0·001 different from the value at 0° C.

The values between 0·0 and 760 mm. pressure are interpolated from the values at 0·0 mm. and 760 mm., which were determined experimentally.

From a careful search of the literature, the authors were unable to find any determination of the density of propane, but they have information at hand that shows beyond doubt that, at 0° C. and 760 mm. pressure, propane is by no means a perfect gas.

Following are some equations that hold only when the partial pressure of the combustible gas and that of the carbon dioxide (at 0° and 760 mm.) produced by the combustion are 95 to 100 per cent of the total pressure. If the partial pressures differ from these, different molecular volumes, depending upon the partial pressures, are used.

Theoretical and Corrected Equations for Combustion of certain Gases.

CH_4, *Theoretical Equation*: $CH_4 + 2O_2 = CO_2 + 2H_2O$.

CH_4, *Corrected Equation*: $0{\cdot}999CH_4 + 2{\cdot}000O_2 = 0{\cdot}994CO_2 + 2H_2O$. 0·999 volumes + 2·000 volumes − 0·994 volumes = 2·005 volumes = contraction.

$0{\cdot}498$ contraction $= CH_4$ $\quad 1{\cdot}005CO_2 = CH_4$

C_2H_6, *Theoretical Equation*: $C_2H_6 + 3{\cdot}5O_2 = 2CO_2 + 3H_2O$.

C_2H_6, *Corrected Equation*: $0{\cdot}990C_2H_6 + 3{\cdot}5O_2 = 1{\cdot}988CO_2 + 3H_2O$. 0·990 volumes + 3·5 volumes − 1·988 volumes = 2·502 volumes = contraction.

$0{\cdot}396$ contraction $= C_2H_6$ $\quad 0{\cdot}497CO_2 = C_2H_6$

CO, *Theoretical Equation*, $2CO + O_2 = 2CO_2$.

CO, *Corrected Equation*: $2{\cdot}000CO + 1{\cdot}000O_2 = 1{\cdot}988CO_2$. 2·000 volumes + 1·000 volumes − 1·988 volumes = 1·012 volumes = contraction.

$1{\cdot}976$ contraction $= CO$ $\quad 1{\cdot}006CO_2 = CO$

C_3H_8, *Theoretical Equation*: $C_3H_8 + 5O_2 = 3CO_2 + 4H_2O$.

C_3H_8, *Corrected Equation*: The observed density of propane, as far as the authors were able to determine, has never been published.

C_2H_4, *Theoretical Equation*: $C_2H_4 + 3O_2 = 2CO_2 + 2H_2O$.

C_2H_4, *Corrected Equation*: $0{\cdot}983C_2H_4 + 3{\cdot}000O_2 = 1{\cdot}988CO_2$, 0·983 volumes + 3·000 volumes − 1·9[illegible] volumes = 1·995 volumes = contraction.

$0{\cdot}493$ contraction $= C_2H_4$ $\quad 0{\cdot}494CO_2 = C_2H_4$

C_2H_2, *Theoretical Equation*: $C_2H_2 + 2{\cdot}5O_2 = 2CO_2 + H_2O$.

C_2H_2, *Corrected Equation*: $0{\cdot}992C_2H_2 + 2{\cdot}500O_2 = 1{\cdot}988CO_2 + H_2O$. 0·992 volumes + 2·500 volumes − 1·988 volumes = 1·504 volumes = contraction.

$0{\cdot}659$ contraction $= C_2H_2$ $\quad 0{\cdot}499CO_2 = C_2H_2$

Gas Analysis Apparatus used by the Authors.

The apparatus used by the authors for the analysis of natural gas and other combustible gases is shown in Fig. 1.

It consists of a 100 cc. burette, which is graduated in tenths of 1 cc., but can easily be read to 0·05 cc. Mercury is used as the trapping fluid. At *f* is the compensating tube. Both the burette and the compensating tube are contained in a water-jacket. At *g* is a mercury manometer.

Attached to the burette by means of rubber tubing is the train of stopcocks which are in turn connected to the caustic potash pipette *a*, the alkaline pyrogallate or phosphorous pipette *b*, the slow combustion pipette *c*, and the alkaline pyrogallate pipette *d*, which contains a supply of nitrogen obtained by removing oxygen from air. The nitrogen is used to sweep out the capillary tubing before an analysis, thereby displacing gas left in the tubing from a previous analysis. Mercury is used in the slow combustion pipette *c*.

Correction of Analyses for Molecular Volume.

Tables VI., VII., and VIII., containing the results of analyses of Pittsburgh natural gas, methane, and carbon monoxide, will serve to show the magnitude of the errors introduced into the calculation from the combustion data when no account is taken of the true molecular volumes of the gases entering into the reactions.

The values for natural gas are calculated by use of the formulæ following. The ordinary equations in which x represents partial methane and y partial ethane serve to obtain the partial pressures of the constituents closely enough for the authors' purposes. Hence—

$$2x + 2{\cdot}5y = \text{contraction},$$
$$x + 2{\cdot}0y = \text{carbon dioxide produced}.$$

From which x and y are calculated.

Table VIII.—*Analyses of Pittsburgh Natural Gas.*

Item.	Sample— 2.16.13.	2.1.13.	9.15.12.	12.1.12.
Volume of sample taken, cc.	31·20	31·55	30·70	31·20
Volume after carbon dioxide absorption, cc.	31·20	31·55	30·70	31·20
Part taken, cc.	31·20	31·55	30·70	31·20
Oxygen added, cc.	91·90	92·80	95·20	90·15
Total volume, cc.	123·10	124·35	125·90	121·35
Volume after burning, cc.	58·10	58·60	62·30	56·45
Contraction, cc.	65·00	65·75	63·60	64·90
Volume after carbon dioxide absorption, cc.	21·90	22·00	27·10	20·45
Carbon dioxide	36·20	36·60	35·20	36·00
Methane from theoretical equation, per cent	84·4	84·5	85·1	85·1
Ethane from theoretical equation, per cent	15·8	15·8	14·8	15·2
Total paraffins from theoretical equation, per cent	100·2	100·3	99·9	100·3
Methane from corrected equation, per cent	83·6	83·7	84·3	84·3
Ethane from corrected equation, per cent	16·3	16·2	15·2	15·7
Total paraffins from corrected equation, per cent	99·9	99·9	99·5	100·0
Difference, total paraffins theoretical minus corrected	0·3	0·4	0·4	0·3

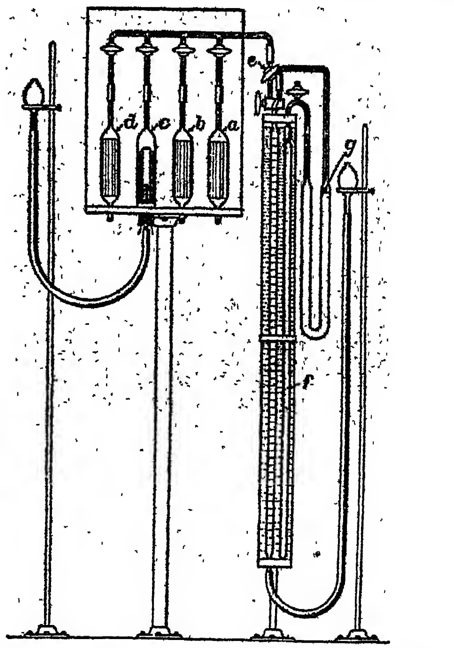


Fig. 1.—Apparatus for Analysis of Combustible Gases.

The partial pressure of the carbon dioxide is obtained in all analyses by dividing the carbon dioxide produced by the combustion by the volume after burning, and multiplying the result by 760.

The corrected equations take the following form for these particular calculations:—

$$2{\cdot}003x + 2{\cdot}5y = \text{contraction},$$
$$0{\cdot}997x + 2{\cdot}0y = \text{carbon dioxide produced}.$$

From which x and y are calculated.

It will be noticed that the molecular volumes of the ethane and of the carbon dioxide produced from it alone have been taken as 1·000, because the partial pressures of the gases are so low that no appreciable error is introduced into the calculation by this procedure. However, if the ethane as shown by the ordinary equations were 25 per cent or higher, as is the case in many natural gases, suitable corrections would have to be made for the molecular volumes of ethane and of carbon dioxide produced by its combustion.

THE SCIENTIFIC WEEK.

(From Our Own Paris Correspondent).

Banana Essence.

Chemists who are clever in discovering in plants and fruits the products which give them their delicate perfume, have not yet been able to determine the nature of the aroma of the banana; M. Kléber, by making a large branch of bananas ripen, then by instilling steam into the strong aromatised fruit, previously peeled, has just been able to obtain a few drops of essence having the characteristic odour of the banana. Acetate of amyl forms the basis of the perfume. It is the first time that the presence of an ether of amylic alcohol has been remarked in a natural essence. Up till now it has always been considered that the presence of these ethers, employed in the manufacture of essences and of artificial perfumes, was bad for health. Nature has just shown us that this is not the case. Acetate of amyl is found naturally in the banana, in small amount, it is true, but completely harmless.

Microbes and the Solar Rays.

M. Roux communicates to the Academy a work of Mdme. Victor Henri, which opens a road for the applications of ultra-violet rays. By exposing, in a certain way, to the rays of mercury lamp, it is seen that beside the microbes that are killed, a certain number continue to exist, which from the fact of irradiation, undergo a great change. Thus, for example, for the microbes of charbon, new races of microbes can be created, which instead of being formed of long rods are round, are completely distinguished by their reactions, and provoke in the animal a malady of quite a different type to that caused by normal charbon. This result brings up the hypothesis that the very numerous different microbes that are to be found in nature are merely the varieties of a small number of primitive types which have become transformed from the effects of a more or less prolonged action of the sun's light and from the conditions of environment.

A Treatment of Charbon.

Dr. Roux, Director of the Pasteur Institute, has made an important communication in the names of Messrs. Louis and Charles Fortmean, of Nantes, concerning a treatment of a great malady of charbon, by subcutaneous injections of sterilised cultures of piocyanic bacilli. These two doctors have treated about 50 patients attacked by charbon, and have only had to register 5 deaths. One single injection generally suffices to cure bacterian charbon. In the rather more serious cases two injections are sufficient.

The Gases of the Nebulæ.

More than ten years ago, the astrophysicians had discovered in the sun a gas unknown on the earth and to which was given the name of helium. This rare gas was discovered in the atmosphere. A few years ago, the science of spectroscopy discovered in the nebulæ, these worlds in a state of formation, the rays of two gases unknown on our globe; to one of these gases was given the name of *Nebulium*, and its ray is ultra-violet. The other gas has not yet received a name; its ray is green. Three physicists of Marseilles, MM. Bourget, Charles Fabry, and Buisson, have succeeded in determining the atomic weight of Nebulium. Nebulium has an atomic weight superior to that of hydrogen and inferior to that of helium. It is about 3; and a remarkable fact is that Nebulium finds its place in the classification of rare gases made by Rydberg. MM. Bourget, Fabry, and Buisson have likewise succeeded in determining the temperature of the Nebula Gion. It is about 15,000°.

Green Coal.

Prof. Labbé, Senator of the department of Orne, has presented a very interesting work of M. Henri Bresson which includes eight hydrographic maps of the Normandy region. By making use of unedited documents of the Agriculture Office, M. Bresson has drawn up the statistic of all the Normandy hydro-electric forces. The green coal of the streams and rivers, so called in opposition to the white coal formed by the torrents and waterfalls of the mountains, can give large quantities of energy. At the present time, in the eight departments of Orne, Rure et Loir, Sarthe, Mayenne, Maine et Loir, Manche, Calvados, and Eure, there are thirty-six hydro-electric installations; but the utilisation of Normandy green coal could be much more considerable.

Threatened Change in the French Metrical System.

The creation of the French Metrical System, the use of which has become almost universal, is one of the finest victories of which France can boast. In the beginning of this month a Bill on the unities of measure was brought before Parliament, which, if passed, would, according to the opinion of very many men competent on the matter, destroy the definitions that are the fundamental principles of this system. There was some fear that this law might be, as it were, smuggled through and voted surreptitiously, and that is exactly what has happened. On April 3rd, in the heat of the tumult caused by the Rochette affair, the Bill was brought before the House and declared. No one asked to speak over it in the general discussion, and when put to the vote it was at once adopted by the deputies, not one of whom knew what it was about. But the veto still remains for the Senate, who will perhaps be better informed and rather more curious as to what they are asked to vote about.

Flies and Mosquitoes Dislike Cod Liver Oil.

A former army veterinary-surgeon, M. Lang, has been making some very interesting experiments in Noumea on flies and mosquitoes, gadflies, &c. These experiments have proved that cod liver oil possesses a very pronounced toxic action on these noxious insects. When it is spread over the surface of stagnant water it kills the larva of these flies much more rapidly than schiste oil, and moreover keeps away other winged insects. The evaporation of this oil is very slow, and it has besides no caustic action on the skin, so that if a horse is smeared over with cod liver oil, in a few minutes it is freed from flies that torment it so much, especially when it is afflicted with wounds and sores, the cure of which is often thus favoured and hastened. But, unfortunately, besides the penetrating and particularly disagreeable odour of cod liver oil, its expense will necessarily limit the employment of this new process.

Two Interesting Scientific Congresses.

Two interesting scientific Congresses are being held this week in Paris. One is the 5th Congress of Physiopathy, which is being held in the Faculty of Medicine, and presided over by Prof. Maurel, of Toulouse. The subject that is to be especially studied at this Congress is the action of physical agents in gout, in ankylosis, and in lupus. The other Congress is to be held at the Sorbonne, and is the fifty-second Congress of the Sociétés Savantes of Paris, and is to be held under the auspices of the Minister of Public Instruction, M. Bienvenu-Martin. In the South of France, on the Azur Coast at Cannes, is also to be held this week the Congress of the International Association of Thalassopathy.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Annual General Meeting, March 26, 1914.

Prof. W. H. Perkin, LL.D., F.R.S., President, in the Chair.

Dr. M. O. Forster drew attention to an article signed by Prof. H. E. Armstrong, appearing in the *Chemical World* for March, 1914, and asked the President the following question:—

"What action have the Council taken or do they propose taking to defend one of their salaried officials from an imputation of inefficiency uttered in a public journal by a Vice-President who has filled the office of President?"

The President, in reply, stated that the matter had received the earnest attention of the Council, who had passed the following resolution:—

"That the Council of the Chemical Society emphatically repudiates the uncalled-for remarks made by Prof. Armstrong in an article in the March, 1914, number of the *Chemical World* which appear to imply literary incompetence on the part of the Editor of the Society's Publications, and offers to Dr. Cain an expression of its continued confidence in and appreciation of his work as Editor";

and that a copy of this resolution has been sent to Prof. H. E. Armstrong, Dr. J. C. Cain, and also to the Editor of the *Chemical World*, asking him to insert the resolution in a prominent position in the next number of that journal.

Dr. G. D. Lander and Dr. F. L. Pyman were appointed Scrutators, and the ballot was opened for the election of Officers and Council for the ensuing year.

The Report of the Council on the progress of the Society during the past year was presented, and the Treasurer made a statement as to the income and expenditure. The adoption of the Report of Council, together with the Balance Sheet and Statement of Accounts for the year ended December 31, 1913, was proposed by Dr. N. V. Sidgwick, seconded by Dr. R. H. Pickard, and carried unanimously.

A vote of thanks to the Auditors was proposed by the Treasurer and acknowledged by Dr. S. Rideal.

Report of Council, 1913—1914.

The Council are gratified to be able to report that the membership of the Society has continued to expand during the past year. On December 31, 1912, the number of Fellows was 3158. During 1913, 164 Fellows were elected, and 2 have been reinstated, making a gross total of 3324. The Society has lost 26 Fellows by death, 40 Fellows have resigned, the elections of 7 Fellows and 1 reinstatement have become void, and 49 Fellows have been removed for non-payment of annual subscriptions.

The total number of Fellows therefore on December 31, 1913, was 3201, showing an increase of 43 over that of the preceding year. On comparing these figures with those given in the previous Report of Council, it will be noticed that the number of elections in 1913 has dropped to the average for the previous six years. The resignations received in 1913 are less by 12 than in the previous year, whilst the number of Fellows removed for non-payment of annual subscriptions still continues very high, notwithstanding the latitude allowed by the Council.

The names of the deceased Fellows, with date of election, are:—Gustavus Anthony Abrines (1890); Matthew Algernon Adams (1877); Edward Louis Barret (1869); J. Carter Bell (1865); William Popplewell Bloxam (1883); Angelo Cantin (1900); Arthur Crozier Claudet (1902); Tom Crossman (1895); James Tudor Cundall (1887); Joseph Davidson (1876); Leopold Mandeville Deane (1886); Frank Standish Findon (1905); Leonard Clifford Green (1908); Sir Walter Noel Hartley (1866); John Heron (1876); John Hunter (1883); Julius Lewkowitsch (1888); Hugh Marshall (1890); George Matthey (1870); Isaac Patchett (1870); Thomas Ebenezer Pye (1906); Mathura Goolab Roy (1900); Christer Peter Sandberg (1870); Walter Shelley Spencer (1887); William Tate (1890); Arthur Wallace (1912).

The number of Honorary and Foreign Members at the end of 1912 was 33. During 1913, Prof. D. P. Konovoloff and Prof. Alfred Werner were elected; the total number of Honorary and Foreign Members at the present time therefore is 35.

In accordance with the announcement made in the Annual Report presented in March of last year, the following Report deals with the work of the Society during the period between that date and the present Annual General Meeting.

The Council offers its hearty congratulations to Prof. George Downing Liveing (elected November 21, 1853) who has completed over sixty years of Fellowship, and to the following, who have reached their Jubilee:—Mr. William Spiller, elected January 15, 1863; John Whitfield, elected November 5, 1863; Prof. John Wrightson, elected February 4, 1864; Mr. Henry Bassett, elected February 18, 1864.

During the year, 355 scientific communications were made to the Society; 253 of these have been published already in the *Transactions*, and abstracts of all have appeared in the *Proceedings*.

The volume of *Transactions* for 1913 contains 2296 pages, of which 2173 are occupied by 238 memoirs, the remaining 123 pages being devoted to the Obituary Notices, the Ladenburg and Van't Hoff Memorial Lectures, the Report of the International Committee on Atomic Weights, the Report of the Annual General Meeting, and the Presidential Address; the volume for the preceding year contained 266 memoirs occupying 2431 pages.

The *Journal* for 1913 contains 5978 abstracts, which extend to 2520 pages, whilst the abstracts for 1912 numbered 5497, and occupied 2264 pages.

In accordance with an announcement made at the last Annual General Meeting, a change has been made in the arrangement of the abstracts, those of Physiological Chemistry and the Chemistry of Vegetable Physiology and Agriculture being included in Part I. instead of in Part II., as heretofore. This has led to approximate equality in the size of the two parts.

	No. of pp. in 1913.	No. of pp. in 1912.
Part I.	1432	1044
Part II. (with indexes) ..	1528	1614

The abstracts may be classified as follows:—

Part I.	Pages.	No. of Abstracts.
Organic Chemistry		1824
Physiological Chemistry		771
Chemistry of Vegetable Physiology and Agriculture		442
	1432	3037
Part II.		
General and Physical Chemistry ..		1401
Inorganic Chemistry		555
Mineralogical Chemistry		159
Analytical Chemistry		826
	1088	2941
Total in Parts I. and II. ..	2520	5978

Following the proposal made by the Deutsche Physikalische Gesellschaft, the Council have decided to request authors to insert either their University, Laboratory, or private address at the end of all papers appearing in the *Transactions*. It is hoped that by this means com-

munication between authors of papers in various journals will be facilitated.

During the past year, advantages have been offered to Fellows of the Society by the reduction in price of certain publications. Arrangements have been made by which Fellows can obtain Vol. I. of the "Literatur Register," by R. Stelzner, at the reduced price of £3 10s. (original price, £4 4s.), provided that not lees than twenty copies of the work be purchased by Fellows. Application for this volume should be addressed to the Honorary Secretaries. Fellows will also be able to purchase the forthcoming Vol. III. of the "International Tables of Physical Constants and Numerical Data at the reduced price of 19s. 3d. (unbound), or £1 2s. 3d. (bound).

Vol. V. of the "Collective Index" of the *Journal* and *Proceedings of the Chemical Society* (1903—1912) has been issued during the year, Part I. ("Author Index") appearing in May and Part II. ("Subject Index") in December. The price of this volume is now £2 to Fellows and £2 10s. to the public.

The Council have decided to offer the Jubilee Volume (giving a history of the Society from 1841 to 1891), which was published at 6s., at the reduced price of 2s. 6d., and also to dispose of a few bound sets of the *Journal of the Chemical Society*, from 1871 to 1900 inclusive (published at £47 10s.), at £20 for the series.

The attention of Fellows is directed to the appearance of a French translation of Vol. IX. of the "Annual Reports." Permission was granted to the Director of the Laboratoire Municipal de Paris for the production of this translation; it was published by Messrs. Hermann et Fils in October last at the price of fr. 7.50.

An intimation has been received from the Faraday Society that this body is prepared to consider the election to membership of a certain number of Fellows of the Chemical Society without payment of an entrance fee.

The *Transactions* for 1913 contain obituary notices of Paul Emile Lecoq de Boisbaudran, Edward Divers, Humphrey Owen Jones, John William Mallet, Henry de Mosenthal, Benjamin Edward Reina Newlands, John Pattinson, Arthur Richardson, John Wade, and William Ord Wootton, who died during 1912, and the Council desire to express their indebtedness to the Fellows who wrote these notices.

The Council also wish to record their thanks to those Fellows who contributed to Vol. X. of the "Annual Reports."

During the past year, the Society has been privileged to listen to Memorial Lectures on Jacobus Henricus van 't Hoff, delivered by Prof. James Walker, and Albert Ladenburg, delivered by Prof. F. Stanley Kipping. In the last Report of Council it was stated that when these two lectures had been delivered the Council would publish Vol. II. of the "Memorial Lectures." This volume has now been issued (price 6s.), and can be obtained from the publishers or from the Assistant Secretary.

The Council have under consideration the desirability of re-issuing Vol. I. of the "Memorial Lectures" (now out of print). To assist them in arriving at a decision in the matter, a circular was issued with *Proceedings* No. 423 inviting those Fellows who would be willing to purchase Vol. I. (price, 10s. 6d.) to notify the Assistant Secretary.

The Council are pleased to announce that the Faraday Lecture is to be delivered by Prof. Svante August Arrhenius, F.R.S., on Monday, May 25, 1914, at 6 p.m., in the Theatre of the Royal Institution (by the courtesy of the Managers). The title of the lecture is "Electrolytic Dissociation."

To meet the convenience of Fellows, the Council decided that a list of the papers to be read at each Ordinary Scientific Meeting of the Society should be advertised in the *Morning Post* on the Wednesday previous to the day of meeting. This list of papers appears on the front page, at the top of the extreme right-hand column.

The stock of apparatus and reagents for the use of Fellows making experiments at the meetings of the Society has been replenished. A list of such apparatus and reagents can be obtained from the Assistant Secretary.

In order to afford Fellows an opportunity of meeting informally, the rooms of the Society were open on the evening of January 15, 1914, when the President and Council were present to receive the Fellows. The Council have decided to provide for a similar meeting on Thursday, April 30, from 8 to 10 p.m.

The Anniversary Dinner of the Society was held at the Whitehall Rooms, Hôtel Métropole, on March 14, 1913, Professor Percy F. Frankland, the retiring President, occupying the Chair. An abbreviated account of the speeches made, together with a list of the names of the Fellows and their guests who were present, appears in the *Proceedings*.

It is with very great pleasure that the Council have to report that a bust of the Right Honourable Sir Henry Enfield Roscoe, by Mr. Alfred Drury, R.A., has been presented to the Society by the friends and former students of Sir Henry Roscoe. The presentation was made before a distinguished company in the Rooms of the Society on November 20, and the bust now adorns the Library.

The meeting of the International Association of Chemical Societies was held in Brussels instead of in London, as previously arranged, in September, the Society being represented by Sir William Ramsay, K.C.B., Prof. Percy F. Frankland, and Prof. Arthur W. Crossley. An abbreviated report of the meeting appears in the *Proceedings*. Thanks to the generosity of M. Ernest Solvay, the Association is now endowed with a sum of Frs. 250,000, in addition to a yearly income of Frs. 37,500 for twenty-eight years, and a site for offices in Brussels.

To celebrate the centenary of the birth of Sir John Bennett Lawes in 1814, and of Sir Henry Gilbert in 1817, it is proposed to erect a Commemoration Laboratory at Rothamsted. Fellows have been invited to respond to the appeal which is being made to raise £6000, this being half the total amount required for the memorial, the other half having been promised in the form of a grant.

Mention was made in the last Report of Council that the sum of £65 4s. had been subscribed by the Fellows of the Chemical Society towards the van 't Hoff Memorial. In April, 1913, the total sum of Fl. 56,000 had been received by the Committee, and a statement with reference to the disposal of this fund is given in the *Proceedings*.

The Council have decided to make a further contribution of £10 to assist the International Commission to prepare the fourth volume of the International Tables of Constants and Numerical Data.

The number of books borrowed from the Library during the year 1913 was 1730, as against 1825 the previous year; of these, 546 were issued by post, as against 491 in the preceding year.

The Additions to the Library comprise: 137 books, of which 68 were presented, 510 volumes of periodicals (representing 241 journals), and 86 pamphlets, as against 135 books, 482 volumes of periodicals (representing 237 journals), and 76 pamphlets last year.

The question of providing for the continuous growth of the Library has been further considered, and a room in the basement has been altered to accommodate 27 rolling book-stacks, estimated to contain 8500 volumes, or twelve years' addition to the Library at its present rate of growth.

From a purely financial point of view, the past year was not so successful as the year immediately preceding it. Notwithstanding the considerable cost of the redecoration and the improvements in the ventilation of the Society's Rooms, there was a balance in 1912 of £176 1s. 7d., whilst in 1913 there is a deficit of £237 7s. 7d. on the year's working. A careful examination of the statement of income and expenditure, however, will show that this need cause no alarm. From all sources, the income for 1913 amounts to £9235 14s. 1d., as against £8120 12s. 3d. in 1912, an increase of £1115 1s. 10d., whilst the corre-

sponding expenditures are £9473 1s. 8d. and £7944 10s. 8d., an increase of £1528 11s. The income, as well as the expenditure, is a record one, and the amount of each has been raised by a common cause. The printing of Volume V. of the Decennial Index alone has added £1378 to the normal expenditure, whilst somewhat over £1000 has already been added to income from its sale. Remembering that Part II. (Subject Index) was only published in December last, it may confidently be anticipated that sales of this volume in the near future may very considerably reduce, if not altogether obliterate, the deficit arising from this source.

Another exceptional expenditure which could not be delayed was the the provision of new iron bookcases for the extension of the Library in one of the basement rooms at a cost of £155 13s. The extra cost of the *Journal* this year was due to the increase of about £63 in Abstractors' fees, and a consequent increase of equal amount in the cost of printing. The cost of the Annual Reports on The Progress of Chemistry for 1912 exceeded that for 1911 by £51. It is to be regretted that the amounts received as Life Compositions and Admission Fees were £141 less than in 1912, when they were, however, considerably above the average.

In the balance-sheet a sum of £168 1s. 10d. appears as an asset, having been paid on account of the International Association of Chemical Societies. This temporary expenditure is owing to the meeting of the Association having been originally arranged to take place in London, but it will shortly be repaid to the Society from the Fund endowed by M. Ernest Solvay to which reference has already been made.

The net income of the Research Fund from investments is about £343, and to this was added £77 16s. 3d., being unexpended grants from previous years which were returned. From this, grants amounting in all to £368 were made, leaving £50 to be added to the balance in hand.

A vote of thanks to the Treasurer, Secretaries, Foreign Secretary, and Council for their services during the past year was proposed by Dr. Bernard Dyer, seconded by Dr. L. T. Thorne, and acknowledged by Sir William Ramsay.

The President then delivered his Address, entitled "Tautomerism." A vote of thanks to the President, coupled with the request that he would allow his Address to be printed in the *Transactions*, was proposed by Prof. R. Meldola, seconded by Prof. W. Jackson Pope, and carried with acclamation, the President making acknowledgment.

The Report of the Scrutators was presented, and the President declared that the following had been elected as Officers and Council for the ensuing year:—

President—W. H. Perkin, Sc.D., LL.D., F.R.S.

Vice-Presidents who have filled the office of President—Henry Edward Armstrong, Ph.D., LL.D., F.R.S.; Alexander Crum Brown, D.Sc., LL.D., F.R.S.; Sir William Crookes, O.M., D.Sc., P.R.S.; Sir James Dewar, M.A., LL.D., F.R.S.; Harold Baily Dixon, M.A., Ph.D., F.R.S.; Percy Faraday Frankland, Ph.D., LL.D., F.R.S.; Augustus George Vernon Harcourt, M.A., D.C.L., F.R.S.; Raphael Meldola, D.Sc., LL.D., F.R.S.; Hugo Müller, Ph.D., LL.D., F.R.S.; William Odling, M.A., M.B., F.R.S.; Sir William Ramsay, K.C.B., LL.D., F.R.S.; James Emerson Reynolds, Sc.D., M.D., F.R.S.; the Rt. Hon. Sir Henry Enfield Roscoe, LL.D., F.R.S.; Sir Edward Thorpe, C.B., LL.D., F.R.S.; Sir William Augustus Tilden, D.Sc., F.R.S.

Vice-Presidents—Herbert Brereton Baker, M.A., D.Sc., F.R.S.; Peter Phillips Bedson M.A., D.Sc.; Horace Tabberer Brown, LL.D., F.R.S.; Charles Thomas Heycock, M.A., F.R.S.; Edmund James Mills, D.Sc., LL.D., F.R.S.; Gilbert Thomas Morgan, D.Sc.

Treasurer—Alexander Scott, M.A., D.Sc., F.R.S.

Secretaries—Samuel Smiles, D.Sc.; James Charles Philip, M.A., D.Sc., Ph.D.

Foreign Secretary—Arthur William Crossley, D.Sc., Ph.D., F.R.S.

Ordinary Members of Council—George Barger, M.A., D.Sc.; the Rt. Hon. the Earl of Berkeley, F.R.S.; Edward John Bevan; Adrian John Brown, M.Sc., F.R.S.; Harold Govett Colman, D.Sc., Ph.D; Arthur Harden, D.Sc., Ph.D., F.R.S.; Thomas Martin Lowry, D.Sc.; Kennedy Joseph Previté Orton, M.A., Ph.D.; Robert Henry Aders Plimmer, D.Sc.; Edward John Russell, D.Sc.; George Senter, D.Sc.; John Millar Thomson, LL.D., F.R.S.

PHYSICAL SOCIETY.

Ordinary Meeting, March 27, 1914.

Prof. Sir J. J. Thomson, O.M., F.R.S., President, in the Chair.

A paper on "*A New Type of Thermogalvanometer*" was read by Mr. F. W. Jordan.

The puff of air from an orifice in an air chamber when the air within is suddenly heated is utilised in this instrument to deflect a small suspended vane. The current to be measured is made or broken through a heater of small thermal capacity in the air chamber and the outrush or inrush of air through the orifice delivers an impulse to the vane. The disturbing effects of extraneous heat and pulsations of external pressure are eliminated by a compensation method. In one instrument of this type the sensibility was 4 mm. per microwatt and the extremity of the throw of the vane was attained in two seconds.

Discussion.

Dr. W. H. Eccles said a good deal of work had been done with convection galvanometers, but Mr. Jordan was the first to measure the pulses produced by suddenly heated filaments. About nine years ago he had made some small instruments consisting of a fine filament connected to heavier leads and mounted in a small glass tube suitable for insertion in the ear. If an interrupted current passed through the filament the observer could hear every pulse produced. The instruments varied in sensitiveness. One which had a platinum filament of 12 ohms resistance could detect 0·0025 ampère, while another, with a platinised quartz filament of 900 ohms, could detect 0·00003 ampère.

Mr. W. Duddell thought the instrument was very ingenious. He asked if the sensitiveness could be increased to measure quantities of energy of the order of a microwatt.

Mr. Jordan, in reply, stated that the fibre was already extremely fine as the inertia was small. He thought the vane could be reduced considerably and the sensitiveness thereby increased without a serious increase in the time of swing.

A paper describing "*An Instrument for Recording Pressure Variations due to Explosions in Tubes*" was read by Mr. J. D. Morgan.

The object of this paper is to describe a mechanical oscillograph for recording the pressure variations which accompany a gas or other explosion in an open tube.

A light steel vane of rectangular form is employed and this is mounted parallel to the explosion tube in a cell presenting a lateral opening to the tube interior. Along three edges the vane is free, and along the fourth edge it is attached to a torsion wire. The vane is made to fit the cell as closely as possible around its edges without touching the sides of the cell. The diagram is produced by a style on a smoked paper strip wrapped around a clock-driven drum, and on the same strip is described a time curve by an electrically-driven tuning fork of known frequency.

To make the instrument dead-beat a dash-pot is mounted on the front of the vane cell and attached to the style.

DISCUSSION.

The CHAIRMAN asked if the author thought all the phenomena shown in some of his curves were features of the original explosion, or if some of them were due to reflected disturbances from the walls and ends of the tube.

Mr. R. APPLEYARD said the different types of curve shown by the author seemed analogous to the oscillatory and aperiodic types of electric discharge. He asked if the author had tried damping with a magnet and copper plate.

Dr. W. WATSON expressed his interest in the instrument. He mentioned with reference to the statement that a diaphragm cannot be made to give a uniform scale, that with a corrugated diaphragm a quite uniform scale of displacement against pressure could be obtained. He believed the author found it advantageous to have considerable inertia in the moving system, and he thought the inertia would play an even more important rôle in defining the extent of the vane's motion under the influence of a sudden expansion than the torsional control. He thought that the effect on the resultant curves of varying the inertia ought to be investigated. He supposed that in the curves shown the disturbance was compounded of what he might call the organ-pipe effect, and another effect due to the time taken by the combustion wave to pass along the tube.

The AUTHOR, in reply, said he had considered electromagnetic damping, but rejected it on account of relative cost. There were, however, grave objections to the use of the dash-pot, which undoubtedly modified the shape of the curves. There was no doubt that the resultant disturbances were compounded of a pressure wave along the tube and a surging of the gas as a whole. It was difficult to separate the effects. In most cases—probably in all—the flame seemed to last as long as the needle was vibrating.

A paper entitled "*The Direct Measurement of the Napierian Base*," was read by Mr. R. APPLEYARD.

The author described a simple apparatus intended to convey to students an idea of the way in which the base *e* of the Napierian logarithms enters into physical problems in a specific case of wide application. A small length of chain is allowed to hang from a loop of thread, and the remaining part of the chain is then pulled aside until the thread is at 45° to the vertical. The curved portion becomes a true catenary when the angle between the vertical and curved portions of chain at the attachment of the loop is 90°. To ensure that this condition is reached, the circle of curvature of the catenary at that point is drawn, and this is found to have a radius equal to the vertical portion. In these circumstances, if the vertical length is taken as unity, and if its lower end is taken as origin, it is shown that e is the sum of the y-ordinate at $x=1$, and the length of curved chain between the point where that y ordinate cuts the curve and the top of the vertical portion. The application of this result to a simple representation of the relationship and meaning of hyperbolic functions was also shown, and it was urged that such functions should be studied from consideration of the catenary rather than from the hyperbola.

DISCUSSION.

The CHAIRMAN supposed the object of the paper was to familiarise students with the properties of the catenary rather than the determination of e, as this was so easily obtained from the formula.

Dr. W. H. ECCLES drew attention to a method of measuring e from the properties of the catenary, which the late Prof. Minchin used to set as a practical problem in the London University examinations.

NOTICES OF BOOKS.

Chemistry and its Borderland. By ALFRED W. STEWART, D.Sc. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1914.

THIS book gives a very interesting account of some recent developments of chemistry, such as can readily be followed by the general reader who is not altogether ignorant of the elements of the science. The relations of chemistry, firstly to the other sciences and then to the industries, are treated in the first chapters, and then recent advances in some special branches which have developed more or less independently are admirably summarised. Thus a chapter is devoted to immuno-chemistry and another to spectroscopic work. Radio-activity and the nature and the transmutation of the elements are considered at some length, and the last chapters are given to the discussion of some chemical problems of the present and the future and to the methods and organisation of chemical research. These later chapters contain some excellent suggestions for schemes for training research chemists, and throughout the book great stress is laid upon the practical and commercial value of pure research. The author writes in a style which is neither too technical nor too elementary, and he is particularly happy in his choice of illustrations and analogies to explain some rather difficult conceptions.

The Co-operation of Science and Industry. By S. ROY ILLINGWORTH, A.R.C.Sc., A.I.C., B.Sc.(Lond.). London: Charles Griffin and Co., Ltd. 1914.

THIS little book, for which Sir Boverton Redwood has provided a fore-word, has been written for business men, with the special aim of pointing out to them the help from a genuine commercial point of view which science can give the Industries. There is certainly need for bringing before the commercial world and the general public the advantages of the co-operation of science and industry, and the author writes clearly and convincingly on the subject. He discusses at some length the problem of the training of scientific and business men, and gives an outline of the excellent scheme of education which has been adopted in Austria. In concluding he shows how the increasing keenness of competition in every branch of commerce must be met by increased efficiency of business men, and points out how essential it is to the welfare of the nation that industry and science should work together hand in hand.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clviii., No. 9, March 2, 1914.

Polymorphism of Camphor.—Fred Wallerant.—When camphor is allowed to crystallise after fusion it is found to be at least quadrimorphic. It is first seen to form cubic crystals, which are transformed as the temperature decreases into rhombohedric crystals, the temperature of transformation being 97°. The ternary crystals are not identical with those obtained by the crystallisation of an alcoholic solution. If one of these large crystals is observed it is noticed that small crystals strongly resembling the primitive crystals form on its edges. The rate of transformation is very small and increases as the temperature is raised. The new crystals are the stable form, for the inverse transformation never takes place. The rhombohedric crystals when cooled to −28° are transformed into new rhombohedric crystals.

Ether-oxides of Carvacrol.—Paul Sabatier and A. Mailhe.—When a mixture of vapours of carvacrol and methanol are passed over oxide of thorium at 420—450°,

a yellow fluorescent liquid is obtained. On fractional distillation this yields a certain amount of mixed oxide of carvacryl and methyl, while the portion passing over above 300° contains oxide of carvacryl. If the catalytic dehydration occurs at a higher temperature prismatic crystals of oxide of dicarvacrylene may be obtained from the resulting liquid. From carvacrol and ethanol small quantities of the mixed oxide of ethyl and carvacryl can be obtained. With carvacrol and phenol mixed oxide of carvacryl and phenyl is obtained, and also oxides of carvacryl and dicarvacrylene.

New Method of Preparing Tricarballylic Acid.—H. Gault.—When oxalocitric lactone is heated to 130—150° at the ordinary pressure carbon dioxide is evolved and a liquid is obtained, which on saponification with dilute mineral acids gives crystallised tricarballylic acid quantitatively. The total yield is about 45 per cent calculated from the oxalacetic ether distilled. If, however, it is referred to the original oxalic ether the yield is only 20 per cent.

Vol. clviii., No. 10, March 9, 1914.

Reduction of Nickel Protoxide and Existence of Suboxide of Nickel.—Paul Sabatier and Léo Espil.—The authors have studied quantitatively the reduction of nickel protoxide by hydrogen, determining not the loss of weight but the weight of water formed. They find that the oxide is reduced more slowly the higher the temperature at which it has been prepared. The reduction is practically proportional to the velocity of the current of hydrogen, and the rate of reduction is an exponential function of the temperature. The progress of the reduction indicates the existence of a suboxide which is slowly reduced by hydrogen at the same temperatures as the protoxide, the final product being free nickel. The presence of water-vapour in the hydrogen diminishes the velocity of reduction.

Determination of Contested Atomic Weights by the Application of the Laws of Transparence of Matter to X-rays.—Louis Benoist and Hippolyte Copaux.—Since transparence towards the X-rays is an intrinsic property of the atom the determination of the equivalent of transparence of an element enables a position on the curve of isotransparence to be assigned to the element, the atomic weight of which is thus fixed. This method of finding atomic weights has the advantage of being entirely independent of any conditions which might make the physico-chemical properties vary. When applied in the case of thorium it shows that the atomic weight is 232, while that of cerium is 140·25.

Preparation of Acetylenic Glycols from their Dimethyl Ethers.—R. Lespieau.—Chloromethylic ether reacts with the acetylenic magnesium derivatives to give ether oxides. In order to demethylate these oxides it is first necessary to fix two atoms of bromine at the double bond, and then subject them for some hours to a current of hydrobromic acid at 100°. The acetins are then obtained by the action of silver acetate, and then saponification gives the brominated glycols. Finally, the bromine is removed by means of zinc powder and alcohol. Thus from $CH_3OCH_2C{\equiv}C.CH_2.CH_2.C{\equiv}C.CH_2.OCH_3$ the new glycol $CH_2OH.C{\equiv}C.CH_2.CH_2.C{\equiv}CCH_2.OH$ can be obtained.

Stereo-chemical Isomers of some γ-Glycols.—Georges Dupont.—Of the two stereochemical isomers into which it is possible to separate acetylenic γ-glycols one should be separable into optical inverses. Generally speaking one is much less soluble in most solvents than the other, and melts about 30° higher. The author has studied the two glycols sym. di-*p*-tolylbutine diol and sym. di-*p*-methoxyphenylbutine diol in order to determine which isomer is which. His experiments have not led to the desired result, but they show that the isomer which is the easiest to obtain is the one which is most likely to prove separable.

Cyclisation of 1.4-Diketones.—E. E. Blaise.—Dipropionylethane can readily be transformed by the action of methyl alcoholic potash into methylethylcyclopentenone, the yield being about 80 per cent. It seems probable that this method of cyclisation is applicable to all acyclic 1.4 non-methylated ketones, the first member of the series acetonylacetone being an exception, for no trace of methylcyclopentenone can be obtained from it.

MISCELLANEOUS.

The firm of Messrs. R. and J. Beck, Ltd., of 68, Cornhill, London, has just produced a binocular microscope which is stated to possess every advantage of a monocular while giving the microscopist the benefit of the stereoscopic relief and comfort of working with two eyes instead of one. It can be instantly converted into a monocular by moving the prism, and judging from the descriptions and illustrations it represents a decided advance in design and efficiency.

MEETINGS FOR THE WEEK.

Monday, 27th.—Royal Society of Arts, 8. (Cantor Lecture). "Some Recent Developments in the Ceramic Industry," by W. Burton, M.A.

Tuesday, 28th.—Royal Institution, 3. "Problems of Physical Chemistry," by W. Wahl, Ph.D.

— Royal Society of Arts, 4.30. "The Administration of Imperial Telegraphs," by Charles Bright.

Wednesday, 29th.—Royal Society of Arts, 8. "The Need for a Better Organisation of Economic and Industrial Resources," by C. R. Enock.

Thursday, 30th.—Royal Institution, 3. "The Last Chapter of Greek Philosophy—Plotinus as Philosopher, Religious Teacher, and Mystic," by The Very Rev. W. R. Inge, D.D.

— Royal Society. "Lack of Adaptation in the Tristichaceæ and Podostemaceæ," by J. C. Willis. "Genetics of Tetraploid Plants in *Primula sinensis*," by R. P. Gregory. "Action of certain Drugs on the Isolated Human Uterus," by J. A. Gunn. "Presence of Inorganic Iron Compounds in the Chloroplasts of the Green Cells of Plants considered in Relationship to Natural Photosynthesis and the Origin of Life," by B. Moore. "Influence of Osmotic Pressure upon the Regeneration of *Gunda ulvæ*," by D. J. Lloyd. "*Glossina brevipalpis* as a carrier of Trypanosome Disease in Nyasaland" and "Trypanosome Diseases of Domestic Animals in Nyasaland, *Trypanosoma pecorum*—Part III., Development in *Glossina morsitans*," by Surg.-Gen. Sir D. Bruce, Major A. E. Hamerton, Capt. D. P. Watson, and Lady Bruce.

Friday, May 1st.—Royal Institution, 9. "A Criticism of Critics," by E. F. Benson, B.A.

— Royal Institution, 5. Annual Meeting.

Saturday, 2nd.—Royal Institution, 3. "Similarity of Motion in Fluids," by T. E. Stanton, D.Sc., &c.

Erratum.—P. 182, col. 2, line 1, *for* "ought to be laid" *read* "ought not to be laid."

THE CHEMICAL NEWS.

VOL. CIX., No. 2840.

NOTE ON THE DETECTION AND ESTIMATION OF HYDROXYLAMINE.

By HAROLD SCHROEDER.

ANGELA (*Gazzetta*, 1893, xxiii., [2], 102) describes a test for hydroxylamine, employing caustic soda and sodium nitro-prusside.

The author found that the somewhat meagre manipulative details given in the above paper were not sufficiently precise to make the test of value in case of a negative result.

It was found as the result of experiment that, by slight modifications in the manipulation, Angeli's test could be rendered rapid and reliable, and could, moreover, be successfully applied to quantitative estimations.

The test liquid is carefully neutralised, using hydrochloric acid and caustic soda. Two cc. of the liquid are then measured into a 5 in. by ⅝ in. test-tube, 1 mgrm. of solid sodium nitro-prusside added, and the whole made alkaline with 1 cc. of N/10 caustic soda. The tube is then shaken and rapidly brought up to 100° C. in a water-bath.

It is advisable to keep fairly close to the above proportions.

In the presence of hydroxylamine at a concentration of 0·01 per cent a characteristic magenta colour develops, as stated by Angeli.

The magenta colour lends itself over to colorimetry, and it is easily possible to estimate small amounts of hydroxylamine by comparing the colour of the test liquid diluted to 50 cc. in a Nessler glass with the colour due to a known amount of hydroxylamine.

The colour can also be matched by a mixture of methyl-orange and phenolpthalein, and a set of standards made once for all. The method has been used by Mumford (*Proc. Chem. Soc.*, 1914).

Frankland Laboratory, University of Manchester.

SIMPLE AND COMPLEX ROTATORY DISPERSION.*

By T. MARTIN LOWRY and T. W. DICKSON.

(Concluded from p. 189).

C. *Anomalous Rotatory Dispersion in Ethyl Tartrate.*

THE following data are taken from an early series of observations on ethyl tartrate, but have not been published previously. The rotations shown are the actual readings for a Cdm Column of the tartrate at 20° C. A much more detailed examination of the form of the dispersion curves for this ester is in progress, but the figures now put forward are sufficiently exact to show that these more complex curves can be represented by a Drude formula containing two terms of opposite sign. The photographic data are taken from some of the earliest observations made by this method and have no claim to be exact; but they have the merit of showing that, as the limit of the visible spectrum is approached, the rotation changes in sign and the ester becomes strongly lævo-rotatory (the lævo-rotation has been traced since as far as −83°); moreover, the curve, as thus greatly extended, adheres closely to the course marked out for it by measurements made in the region in which visual observations can be taken.

TABLE I.—*Anomalous Rotatory Dispersion in Ethyl Tartrate.*

$$\delta = \frac{132{\cdot}78}{\lambda^2 - 0{\cdot}026} - \frac{103{\cdot}05}{\lambda^2 - 0{\cdot}061}.$$

		Observed.	Calculated.	Calc.-Obs.
Cd red ..	6708	50·06°	50·26°	+0·20
Zn red ..	6364	51·03	50·78	−0·25
Na yellow	5893	53·32	53·32	±
Cu yellow	5782	53·60	53·63	+0·03
Hg yellow	5780	53·69	53·63	−0·06
Cu yellow	5700	53·58	53·74	+0·16
Hg green	5461	53·42	53·36	−0·06
Cu green	5219	51·49	51·41	−0·08
Cu green	5154	50·62	50·50	−0·12
Cu green	5105	49·53	49·72	+0·19
Cd green	5086	49·44	49·35	−0·09
Cd blue ..	4678	35·64	35·69	+0·05
Hg violet	4359	10·79	10·76	−0·03
Photographic observations :—				
	4737	40	39	−1
	4443	20	19	−1
	4250	0	−3	−3
	4133	−20	−22	−2
	4034	−40	−42	−2

It should be noticed that the formula given above can be interpreted in a variety of ways. The two free periods are both beyond the limits of observation, and the anomaly is therefore not due to Cotton's phenomenon. But the form which the equation takes might be due to two vibrations of unequal period and opposite activity, as suggested by R. W. Wood; to the superposition of two "partial-rotations," as investigated by Tschugaeff in the case of menthyl camphor-β-sulphonate; or to the actual presence of two distinct substances, as in the mixtures of turpentine and camphor, which were shown by Biot to give rise to anomalous rotatory dispersion.

D. *Dynamic Isomerism as a Cause of Anomalous Rotatory Dispersion.*

Whilst there is no reason to doubt that anomalous rotatory dispersion (especially in compounds containing several asymmetric carbon atoms) may be due to the superposition of partial rotations of opposite sign, there is good reason to think that this phenomenon is more commonly produced by the presence of two or more different compounds in a liquid which nominally contains only one optically-active constituent. This view was expressed by Arndtsen in 1858, as a means of interpreting his own observations on the anomalous rotatory dispersion in tartaric acid. After quoting Biot's experiments on the anomalous rotatory dispersion in mixtures of turpentine and camphor, he writes:—

"One then might regard tartaric acid as a mixture of two substances differing only as regards their optical properties, of which one had a negative rotatory power, the other a positive rotatory power, these rotations varying in different proportions with the refrangibility of the light" (*Ann. Chim. Phys.*, 1858, liv., 421).

Two modifications of a substance, differing in their optical properties but identical in chemical behaviour, may be produced—

(i.) By association with the solvent;
(ii.) By polymerisation of the solute; or
(iii.) By isomeric change.

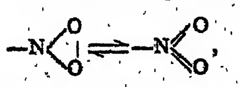
In order that the chemical properties of the two modifications may be the same, it is necessary that these changes should be reversible; if this condition is not fulfilled, the two modifications could indeed be separated by ordinary

* A Contribution to a General Discussion on "Optical Rotatory Power," held before the Faraday Society, March 27, 1914

methods of fractionation, and the liquid would differ in no essential point from Biot's artificial mixtures of dextro- and lævo-rotatory compounds.

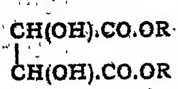
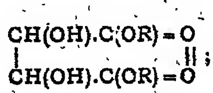
The way in which a homogeneous solid may give rise to a mixture on fusion or dissolution may be illustrated most readily in the case of the reversible isomeric changes, which have been very fully studied under the name of *dynamic isomerism*. It has been shown, for instance, that nitro-camphor changes over in solution (to the extent of about one-sixth) into an acidic isomeride, of opposite rotatory power and probably of unequal dispersive power, thus giving rise to just the right conditions for anomalous rotatory dispersion. The anomaly would here be due to a chemical change belonging to type (iii.), *reversible isomeric change*. All the phenomena would be the same if one of the modifications existed, *e.g.*, in a bimolecular form as $[C_{10}H_{15}NO_3]_2$, but the anomaly would then be attributed to (ii.) *reversible polymeric change*. (The acidic form of nitrocamphor might be expected to polymerise in nonionising solvents, compare acetic in benzene $[C_2H_4O_2]_2$). Further, one of the modifications might combine with the solvent (there is good reason for thinking that normal nitrocamphor forms unstable compounds when dissolved in benzene and its homologues); in this case the phenomena would be precisely similar, but the anomaly might be classified as due to a change of type (i.) *association with the solvent*.

In the case of nitrocamphor, isomeric change in solution is sufficiently slow to give rise to the phenomenon of *mutarotation*, and it was by observations of this kind that this change was first detected. But it is to be expected that anomalous rotatory dispersion may reveal many reversible changes which reach a condition of equilibrium too quickly to be detected or studied by dynamic methods. In the discussion on Pickard and Kenyon's paper (*Proc. Chem. Soc.*, Nov. 20, 1913), it was suggested by one of us (T. M. L.) that a change of type such as that involved in the conversion of tervalent into pentavalent nitrogen—

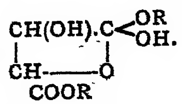
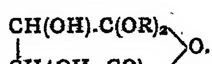


might be demonstrated by observations of anomalous rotatory dispersion in an optically-active nitro-compound, even if too elusive to be detected by any other method. So also an elusive polymerisation may reveal itself by producing anomalous rotatory dispersion in an active liquid, just as the polymerisation of nitrogen dioxide $2NO_2 \rightleftharpoons N_2O_4$ manifests itself in the varying colour of the gas or liquid, although the changes are too rapid to admit of the separation of the two components by ordinary methods.

In the special case of the tartrates, Armstrong and Walker (*Proc. Roy. Soc.*, 1913, A. lxxxviii., p. 399) have suggested four formulæ for the isodynamic forms of the acid. In the tartaric esters, two of these modifications might appear as dynamic isomerides—

I.  II. 

but the third would probably decompose into an alcohol and an acid-ester, whilst the fourth would be a stable isomeride, not readily convertible into the other forms—

III.  IV. 

As a matter of fact, ethyl tartrate appears to be a commonplace mixture which can be fractionated by ordinary methods into portions which differ widely in their rotatory power for violet light; it may therefore contain the fixed ester IV. in addition to various labile forms of the ester I. But methyl tartrate, which is a well-defined crystalline compound and resists fractionation, also shows anomalous dispersion; this cannot be attributed to ordinary static isomerism, but may be due to a dynamic isomerism of one of the more elusive types, in which the change of structure is too rapid to manifest itself by mutarotation in the freshly-prepared solutions. Some such labile isomerism, involving little more than a rearrangement of residual affinities, must also be postulated to account for the anomalous rotatory dispersion in the simple esters described by Pickard and Kenyon. Even more emphatically are the coarser types of isomerism ruled out in the case of naphthylmethylcarbinol, $C_{10}H_7.CH(OH).CH_3$, the anomalous dispersion in which (if not due to polymerisation) may perhaps depend on the concrete existence of two or more of the many varieties of the aromatic nucleus postulated by organic chemists during the past fifty years.

E. *Simple and Complex Rotatory Dispersion.*

In the preceding pages it has been shown that every case of rotatory dispersion that has been investigated can be represented by means of Drude's equation. Instead of making a distinction between "normal" and "anomalous dispersion," it would be more satisfactory at the present time to distinguish in the first place between *simple rotatory dispersion*, which can be expressed by the equation—

$$\alpha = \frac{k}{\lambda^2 - \lambda_0^2}$$

and *complex rotatory dispersion*, which must be expressed by an equation containing two or more terms, thus:—

$$\alpha = \frac{k_1}{\lambda^2 + \lambda_1^2} + \frac{k_2}{\lambda^2 + \lambda_2^2} + \ldots$$

A complex rotatory dispersion may become "anomalous," as R. W. Wood has pointed out, whenever the range of observations covers the region between two absorption bands. This statement includes the anomalous dispersion of Cotton's phenomenon, where the anomaly is observed in the region between an accessible band and an inaccessible band in the remote ultra-violet.

A second form of anomalous dispersion may be produced by two bands on the ultra-violet side of the region under observation, provided that these are associated with rotations of opposite sign. This anomaly is only to be looked for in the case of optical rotations, since negative magnetic rotations are confined to a small range of metallic compounds and have never been detected in optically-active organic compounds.

GENERAL CHARACTERISTICS OF PAPERS PRODUCED FROM HEDYCHIUM CORONARIUM.

By CLAYTON BEADLE and HENRY P. STEVENS.

So much practical work has been done in producing papers of different kinds and qualities from this fibre, in many cases on commercial scales in paper mills, and as this fibre has received so much attention at the hands of the paper trade, we think the time has now arrived to refer to these productions somewhat in detail.

The first papers which we produced experimentally were more or less of the Kraft or strong wrapping paper description. As soon as we discovered the cause of the self-sizing we produced papers from parchments to blotting paper. When some papers had been produced on quite a laboratory scale they were reproduced on a small machine as waterleaf, rosin-sized, and some even sized with gelatin. It was soon discovered that the addition of rosin size and alum by way of sizing had no beneficial effect, in fact

alum had a harmful effect. The only beneficial effect could be got in extreme cases, where the whole of the glutinous matter had been removed from the fibre by washing and a sizing result obtained by the addition of rosin and alum. Even here the benefit was doubtful. We soon realised that the proper way of procedure would be to leave all the constituents in, that is if strong sizing and strong paper is required. If softer and more opaque paper is required the addition of some clay will bring about the desired result.

When, however, we resorted to bleaching we made a range of white papers, some of them suitable for fine cigarette papers, others of a softer nature suitable for fine printing, others with excellent bibulous qualities suitable for blottings. Their general appearance is that of good cotton paper. It is not, however, in the direction of bleach fibre that we consider the fibre has its chief value, as we subsequently discovered that there were easier modes of dealing with the fibre.

We ran off some paper on the machine, a portion of which was unbleached, a portion half bleached, and a portion fully bleached. Some of it was unwashed. Portions were washed, run off in the form of waterleaf. To other portions rosin size and alum were added. For the most part the physical qualities of these papers have been described. We produced anywhere from thick substances down to thin silky tissues of 24 grms. to the square metre. These thin tissues, as also some thicker paper 42 grms. to the square metre, had a breaking strain up to 10–11 kilometres in the machine direction—in fact, they are the strongest papers we have so far examined.

On a more extensive scale we produced paper by light boiling in 5 per cent soda with a subsequent bleaching with 5 per cent bleaching powder and very light beating. This was produced at one of the leading paper mills, some of it without anything added, some with rosin size and alum, and the rest, after rosin sizing, was run through a gelatin bath and gelatin sized. All these papers were very excellent. The material was only partially washed in the beater, so the result of the unsized was a semi waterleaf effect. This paper was valued on the market at between £14 and £15 a ton, and is very excellent for small hands, linings, casings, and certain forms of wrappings. A paper made somewhat in this way was thoroughly tested for copying purposes. We found that excellent impressions were obtained in the ordinary way, and it has about the colour, substance, feel, and flexibility required for the manufacture of copying books. By slightly altering our methods, we obtained a silkier feel, such as is obtained with thin Japanese tissues. There is no point in gelatin sizing this class of paper, but it is interesting to note that the web can be passed through a gelatin trough, even when it is a very thin tissue, without giving any difficulty or showing any liability to breakage.

A further trial was made in one of the leading paper mills with a very light boil and light wash in the beater with the roll up for one hour, and the second hour the roll was slightly put down to brush. The paper was put over the paper machine, the stuff was allowed to remain hairy in consequence of the fibro-vascular bundles largely remaining in an unbeaten state. This paper was pronounced equal to and in some respects better than Manila. It was thoroughly tested electrically and physically by a large firm of cable manufacturers, and pronounced to be suitable for the insulation of electric cables. This came as a surprise to us, because when made there was no intention of producing a paper for this purpose. It was quite an afterthought to have it tested in this way. This particular type of hairy Hedychium paper has taken on with members of the paper trade. It has a strong look and feel, and handles exceedingly well. It folds and stands the crumpling test as well as any Manila paper, and has good elastic qualities.

Hedychium can be used practically for all kinds of packing papers. It has been made up for bags of different descriptions. Browns of all descriptions have been made from the commonest to the finest qualities. It possible to so manipulate the fibre as to produce a dark coloured brown of the ordinary old-fashioned type, or of any grade up to kraft and Manila, without the addition of anything. It comes in for butter papers as well as for cartridge papers. Cutlery papers are a special line usually made from Manila, to which this fibre is well adapted. Bags for bank cashiers are frequently made from Manila; Hedychium is equally adaptable. Much of the earlier Hedychium paper was made of the greaseproof description. The greaseproof tests were applied to these in comparison with greaseproof papers now upon the market and found to stand all the necessary tests; in fact, it can be made to border upon vegetable parchments. It is also suitable for leather boards, millboards, and mill wrappers.

The paper which stood the crumpling and folding test best was a semitransparent all-hedychium machine-made greaseproof paper; it stood six times crumpling and 1000 rubbing, withstanding pinholes; this is an exceedingly severe test.

We have recently studied the question of coloured papers. Generally speaking, the basic dyes and the diamine colours give good results. The following is a list of dyes that have been tested with satisfactory results:—

Yellows.—Papier Yellow, R., G. G., Metanil Yellow, Auramine, Diamine Fast Yellow, Brilliant Yellow.

Red.—Congo, Diamine Scarlet B., Eglantine, Fast Diamine Scarlet 4 B., Saffranine G. extra, Diamine Red, Brilliant Bordeaux R., Brilliant Croceine M. OO.

Black.—Coal Black B., Paper Black T.

Blue.—Diamine Sky Blue F.F., Victoria Blue B., Alizarine Cyanole, Diamine Fast F.F.B., Pure Soluble Blue.

Brown.—Diamine Catechine 3 G., Bismarck Brown F. concentrated, Diamine Brown M.

Green.—Imperial G. 1, Brilliant Green Crystals extra.

Prussian blue has given good results, and on account of the peculiar absorbent nature for mineral matter, it is likely that most of the pigments can be used to advantage. Other trials with pigments are now in progress.

Coming now to the question of paper yarn, which in itself is an important industry, and likely to become more so in the near future, we have already referred to the suitability of Hedychium paper for the manufacture of paper yarns on account of its great strength and elasticity. We ran off some reels of Hedychium paper some 42 grms. per square metre, and some tissue as thin as 25 grms. These papers were run over paper yarn machines, and the yarn so produced tested in comparison with paper yarns on the machine made from strong Swedish grass. The result was at least equal to the best yarns produced from kraft. The mineral absorbent power of Hedychium renders it possible to greatly extend its use.

To sum up, we give an alphabetical list of papers for which Hedychium can be used without admixture of other fibres:—

Backing papers. Bag papers of all descriptions. Box boards. Browns of all descriptions. Butter papers. "Caps." Carpet felt papers. Cartridge papers. Casings. Coloured papers. Copyings, Cutlery papers. Duplex papers. Engine boards. Envelope papers (many kinds). Fly papers. Foil papers. Glazed boards. Greaseproof papers. Grocery papers. Hosiery papers. Kraft papers. Leather boards. Manilas. Mill boards. Mill wrappers. Paper yarn. Parchment (imitation). Pin and needle papers. Portmanteau boards. Printings (many kinds). Railway tickets. Sampling papers. "Shops." "Skips." Tea papers. Tissues. Tobacco papers. Toilet papers. Tube papers. Wrappings.

Its use, of course, can be extended by admixture with other materials, but the above would cover a very large market.

THE SCIENTIFIC WEEK.

(*From Our Own Paris Correspondent*).

CATS THAT ARE NOT AFFECTED BY THE COLD.

In order to get rid of the multitude of rats that infested the freezing establishments of the town of Pittsburg, in Pennsylvania, the owners were obliged to procure some cats having a very thick white fur and coming from the Polar regions, for the ordinary domestic cats of the district were paralysed and often died owing to the low temperature of the rooms in which the perishable goods are preserved. These white polar cats, like the white polar bears, seem to resist any degree of cold, however low, and their very thick whiskers make them look very formidable indeed; they are at the same time excellent rat-catchers, so that the depôts of Pittsburg were promptly cleared of their terrible pest.

NEW PETROLIFEROUS BEDS.

A French professor, M. Durandin, has just imagined a somewhat curious method for discovering petroleum beds. M. Durandin does not make any soundings nor preparatory prospections. He only finds out the typonymy of the different localities of a region. He has thus been fortunate enough to discover petroleum where the names of the places recalled the fact that this matter had been known by the natives in former times. In Africa, M. Durandin, by the help of this method, has been able to find out several petroleum beds. He has proceeded in the same way in Indo-China and in Upper Tonkin. In those villages and districts the names of which recalled wax-oil, such as Louang-Prabang, Prof. Durandin has discovered petroleum. This typonymic method has likewise been applied by the gold-seekers when searching for the precious metal. Several localities in France, such as Aurière, St. Sulpice-Laurière, &c., recall by their names the fact that, in these regions there were formerly gold diggings or exploitations.

THE BROMIDES OF THE OCEAN.

Very interesting researches have just been made by M. Louis Chelle, Professor of the Faculty of Medicine of Bourdeaux, concerning sea-water bromides. The different samples of sea-water collected by M. Chelle contain from three to four thousandths of the total quantity of chloride. But the relation of the bromide to the chloride seems to be a constant equal to about four-thousandths for all the seas of the globe, excepting for the Black Sea and for the Baltic. M. Louis Chelle has just searched out in the *Bulletin de l'Institut Oceanographique* what is the quantity of bromine contained in the seas and the oceans. As is known, the total of the marine waters of the globe occupies a volume of about 1200 millions of cubic kilometres. These waters containing about the ten-thousandth part of their weight of bromides, it is easy to deduce from this that the totality of oceans contains 120,000 milliards of tons of this salt; that is to say, 80,000 tons per head for each inhabitant of the globe. If then every human being used a kilogrm. of this salt every year it would take 80 millions of years to use up these reserves. The density of melted bromide of sodium being about 3, the volume of this salt of the sea is represented by 40,000 milliards of cubic metres. If the totality of this salt were uniformly spread over the surface of France (536,408 square kilometres), it would occupy a height of 73 metres. But thus it is easy to appreciate the enormous stock of bromide reserves contained by the Neptunian world.

University of London, King's College, Strand, W.C.—*Advanced Lectures in Chemistry*.—A course of two public lectures on "La Catalyse et mes Divers Travaux sur la Catalyse" will be given by Prof. Paul Sabatier, of the University of Toulouse, on Thursday, May 14, and Friday, May 15, 1914, at 5 p.m.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, April 2, 1914.

Prof. W. H. PERKIN, LL.D., P.R.S., President, in the Chair.

THE PRESIDENT announced that the Council have appointed the following Committees for the year 1914—1915:—

Finance Committee—Messrs. E. G. Hooper, G. T. Moody, Sir Edward Thorpe, Sir William A. Tilden, and the Officers.

House Committee—Messrs. Horace T. Brown, R. Messel, J. E. Reynolds, J. M. Thomson, Sir William A. Tilden, and the Officers.

Library Committee—Messrs. B. Dyer, W. Gowland, A. Harden, J. T. Hewitt, C. A. Keane, A. R. Ling, T. M. Lowry, R. Meldola, E. J. Mills, J. M. Thomson (Chairman), Sir William A. Tilden, J. A. Voelcker, the Editor, and the Officers.

Publication Committee—Messrs. H. B. Baker, J. N. Collie, F. G. Donnan, B. Dyer, M. O. Forster, T. M. Lowry, F. B. Power, G. Senter, and the Officers.

Research Fund Committee—Messrs. H. B. Baker, W. R. Bousfield, Horace T. Brown, H. B. Dixon, J. J. Dobbie. F. G. Donnan, M. O. Forster, P. F. Frankland, W. J. Pope, W. Palmer Wynne, and the Officers.

Messrs. S. Bate, A. H. Hay, and F. A. Pickworth were formally admitted Fellows of the Society.

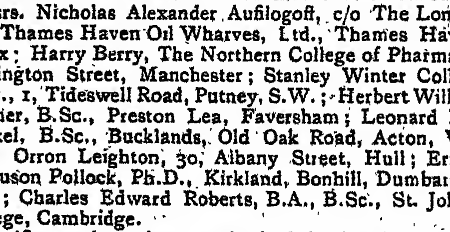
Certificates were read for the first time in favour of Messrs. Nicholas Alexander Aufilogoff, c/o The London and Thames Haven Oil Wharves, Ltd., Thames Haven, Essex; Harry Berry, The Northern College of Pharmacy, Burlington Street, Manchester; Stanley Winter Collins, B.Sc., 1, Tideswell Road, Putney, S.W.; Herbert William Cremer, B.Sc., Preston Lea, Faversham; Leonard Eric Hinkel, B.Sc., Bucklands, Old Oak Road, Acton, W.; John Orron Leighton, 30, Albany Street, Hull; Ernest Ferguson Pollock, Ph.D., Kirkland, Bonhill, Dumbartonshire; Charles Edward Roberts, B.A., B.Sc., St. John's College, Cambridge.

Certificates have been authorised by the Council for presentation to ballot under By-law I. (3) in favour of Messrs. Edward Godfrey Bryant, B.A., B.Sc., Grey Institute, Port Elizabeth, S. Africa; Alfred Cornwell Harrison, Penhalonga, Rhodesia, S. Africa.

Of the following papers those marked * were read:—

*92. "*The Constitution of the Glycerylphosphates. The Synthesis of α- and β-Glycerylphosphates.*" By HAROLD KING and FRANK LEE PYMAN.

Pure salts of α- and β-glycerylphosphoric acids have been prepared. For the preparation of the β-salts, α dichlorohydrin was combined with phosphoryl chloride (compare Tutin and Hann, *Trans.*, 1906, lxxxix., 1749), giving *calcium bis-s-dichloroisopropylphosphate*, which on hydrolysis with sodium carbonate yielded sodium β-glycerylphosphate,—



This salt was identical with Poulenc's crystalline sodium glycerylphosphate of commerce, which must consequently be the β-salt. The identity of the two salts was confirmed

by the comparison of the properties of the calcium, barium, brucine, and quinine salts prepared from each of them.

An attempt to prepare the α-salts in an analogous manner was unsuccessful, but these salts were readily obtained by the action of α-monochlorohydrin on trisodium phosphate in cold aqueous solution:—

$$HO{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2Cl + (NaO)_3PO \rightarrow HO{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}O{\cdot}PO(ONa)_2.$$

Several salts of the α-acid were prepared and characterised.

The results of previous investigators were discussed.

DISCUSSION.

Dr. PLIMMER asked Dr. Pyman how the analyses of the glycerlphosphates, which he described, had been effected. In his experience of the analysis of organic phosphorus compounds, the values obtained for carbon, by combustion by both dry and wet methods, were always too low.

*93. "*The Viscosity of Sulphuric Acid.*" By ALBERT ERNEST DUNSTAN.

Some years ago (Dunstan and Wilson, *Trans.*, 1907, xci., 85) a series of determinations of the viscosities of aqueous sulphuric acid solutions at 25° was undertaken with the object of finding the maximum point. Owing to the kindness of Prof. A. F. Joseph, it was discovered that a constant numerical error had been made in calculating the values of the viscosity coefficients. Consequently, the numbers given on p. 85 of the above reference should be multiplied by 0·2325.

In the meantime, several papers have appeared on the viscosity of sulphuric acid, and as the results apparently fall on two distinct curves, it was thought desirable to repeat some of the measurements, both at 25° and at other temperatures, and to ascertain which of these two sets of results is the more accurate.

The figures up to date are as follows:—

Observer and reference.	Viscosity.	Temp.
Kremann and Ehrlich (*Monatsh.*, 1907, xxviii., 831)	0·618	0·0°
Drucker and Kassel (*Zeit. Phys. Chem.*, 1911, lxxvi., 373)	0·4843	0·0
Poiseuille (*Ann. Chim. Phys.*, 1843, [2], vii., 50)	0·3195	11·2
Drucker and Kassel (*loc. cit.*)	0·2694	15·0
Graham (*Phil. Mag.*, 1862, xxiv., 238)	0·2193	20·0
Bergius (*Zeit. Phys. Chem.*, 1910, lxxii., 357)	0·1915	25·0
Pound (*Trans.*, 1911, xcix., 708)	0·210	30·0
Kremann (*loc. cit.*)	0·172	33·0
Kremann (*loc. cit.*)	0·076	63·5
Drucker (*loc. cit.*)	0·0503	76·5

The values found by Kremann and Ehrlich and by Pound lie well above those of Drucker, Graham, and Poiseuille.

In the experiments here recorded, the strength of the sulphuric acid was determined by gravimetric and volumetric methods, and also by means of the densities of its diluted aqueous solutions.

The mean of eight concordant analyses was 100·3 per cent (calculated as H_2SO_4), with a mean error of 0·2 per cent.

The method which was adopted for obtaining values of the viscosity of the 100 per cent acid consisted in interpolating on a viscosity-concentration curve ranging from 96 to 100·3 per cent.

The results are as follows:—

Temperature.	Viscosity of— 100·3 per cent H_2SO_4.	99·8 per cent H_2SO_4.	98·2 per cent H_2SO_4.	96 per cent H_2SO_4.
13·8°	0·371	0·342	—	—
25·0	0·239	0·224	0·220	0·190
50·0	0·109	0·102	0·0954	0·0943
70·0	0·0632	0·0657	0·0598	—
90·0	0·0433	0·0410	0·0403	0·0399

whence for the 100 per cent acid:—

Temperature.	Viscosity.
13·8°	0·360
25·0	0·235
50·0	0·106
70·0	0·0635
90·0	0·0425

The value thus found at 25° is rather less than tha which was previously obtained, but it will be seen that the iew values agree excellently with those of Kremann.

*94. "*Tautomerism, Desmotropy, and Dynamic Isomerism.*" By THOMAS MARTIN LOWRY.

The question asked by Prof. Meldola at the close of the 'resident's Address to the Annual General Meeting of the Chemical Society suggests that a short statement in refer:nce to the nomenclature of the subject might be welcomed iy some Fellows who have not had an opportunity of ionsulting the earlier literature.

Briefly, it may be said that all the essential facts in 'eference to the conception of *equilibrium between isomerides*, as described so lucidly by the President in his Address, are set out in Butlerow's classical, but almost 'orgotten, paper "Ueber Isodibutylen" (*Annalen*, 1877, :lxxxix., 44). They were applied by him to explain the behaviour of substances such as cyanic and hydrocyanic acids, which yield two series of derivatives; these were 'egarded by Butlerow as mixtures of isomerides in equi.ibrium, to which no definite formula could be assigned, "since molecules of two or more isomeric varieties would always be present." The name *dynamic isomerism* was 'ntroduced in 1899 (*Trans.*, lxxv., 235), as a paraphrase of Butlerow's description of "a condition of equilibrium depending on incessant isomeric change"; but the adjec:ive *isodynamic* had already been suggested by Armstrong n 1889 (Watts' Dictionary, "Isomerism") to describe those isomerides "which change their type with exceptional facility in the course of chemical interchanges." The word *metameric* had been used in this sense in 1833 by Berzelius to describe isomerides which were readily converted into one another, but the usefulness of the word was destroyed by a misguided attempt to transfer it to another usage.

The hypothesis of *tautomerism* was introduced by Laar in 1885 (*Ber.*, xviii., 648) to account for the facts which had already (as time has shown) been explained adequately by Butlerow. The clearest statement of what tautomerism means, however, is found in a subsequent paper (*Ber.*, 1886, xix., 730), in which Laar sets out the points in which his views differ from those of Butlerow. Laar asserts that, in every case of tautomerism, the different formulæ suggested by the reactions of the substance represent, "not isomeric, but identical bodies"; the term cannot, therefore, be applied to any case of isomerism, however readily the isomerides may be converted into one another. Further, he repudiates the chemical analogy of dissociation, which Butlerow had suggested, and quotes instead the views of Maxwell and of Wiedemann on the molecular vibrations which give rise to light.

It is impossible to say whether tautomerism exists; but it has at least been proved by the work of Knorr that the two substances represented by the formulæ—

$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO_2Et \text{ and } CH_3{\cdot}C(OH){:}CH{\cdot}CO_2Et$$

are not tautomeric, but have a real existence as well-defined isomeric compounds, which only change into one another under definite physical and chemical conditions. They have, in fact, a right to be described as isomerides, in just the same sense as ammonium cyanate and carbamide, two fortunate compounds which have hitherto escaped condemnation, although equally guilty of undergoing reversible isomeric change and of yielding two series of derivatives.

The word *desmotropy* was introduced by Jacobson (*Ber.*, 1887, xx., 1732, footnote; 1888, xxi., 2628, footnote) in 1887, when it had become evident that Laar's theory o

tautomerism had broken down completely in the very case to which it had been most frequently applied, namely, the labile isomerism which results from the contiguity of a double bond and an acidic hydrogen atom. Jacobson adopted the view "that the known forms of such compounds are to be represented by a definite grouping of atoms, which in certain reactions passes over into an isomeric grouping by a rearrangement of bonds consequent upon the displacement of a hydrogen atom"; it was to express this view that the word "desmotropy" was introduced. If used in this sense, to describe the labile isomerism produced by the mobility of a hydrogen atom, it might be of real value; unfortunately, the meaning of the word was tampered with by Hantzch and Hermann (*Ber.*, 1887, xx., 2802), and, as an inevitable consequence, it has become ambiguous, and has ceased to be clearly significant.

DISCUSSION.

Dr. FORSTER expressed regret that Dr. Lowry's remarks failed to clear up the confusion attending the words in question. Having stated that no case of genuine tautomerism exists, and that he deplored the association of an incorrect meaning with any word, Dr. Lowry might have declared that, in his opinion, use of this word should be discontinued. In Dr. Forster's view, the word isodynamic was unsuitable, because it suggested equal, or similar, force or motion, whereas one of the commonest features of such pairs is that one member changes far more rapidly than the other.

Dr. LOWRY replied that the word "tautomeric" should be withdrawn in all cases of proved isomerism, and might with advantage be abandoned altogether by those who no longer accepted Laar's hypothesis. The familiar words "isomerism" and "isomeric change" should be used whenever they expressed the essential facts; if these were not sufficient, the term "dynamic isomerism" might be used to distinguish the more labile varieties of isomerism; in view of the difficulty of re-introducing the word "metameric" in its original sense, the labile compounds themselves were best described as "isodynamic," for example, the two substances isolated by Knorr could be referred to as "isodynamic forms" of the ester.

95. "*The System: Ethyl Ether—Water—Potassium Iodide—Mercuric Iodide. Part III. Solutions Unsaturated with respect to Solid Phases in the Four-component System.*" By ALFRED CHARLES DUNNINGHAM.

Liquids unsaturated with respect to solid phases can exist either as one, two, or three layers.

Curves have been determined experimentally for the series of three conjugate liquids, and from these the nature of the equilibria underlying the formation of three layers has been deduced.

The conditions under which two and three layers can separate in the system were fully discussed.

96. "*The Velocity of Saponification of the Acyl Derivatives of the Substituted Phenols. Part I. Phenyl Benzoate.*" By HAMILTON McCOMBIE and HAROLD ARCHIBALD SCARBOROUGH.

The velocity of saponification of phenyl benzoate by alcoholic potassium hydroxide at 30° has been studied with reference to the influence of the initial concentration of both the ester and the alkali.

The value of K was found to be independent of the initial concentration of either of the reacting substances, a mean value, K=0·00428, being obtained as the result of five series of determinations, each series representing twenty-five readings.

The reaction, as a whole, was found to be bimolecular; the van't Hoff and Noyes equations for determining the order of the reaction proved that the reaction was unimolecular with regard to the initial concentration of the ester or the alcoholic potassium hydroxide.

97. "*A General Method for the Preparation of Glyoxals and their Acetals.*" By HENRY DRYSDALE DAKIN and HAROLD WARD DUDLEY.

Ethyl diethoxyacetate and ethyl acetate react smoothly with sodium to give ethyl γ-diethoxyacetoacetate. The latter substance on hydrolysis with potassium hydroxide gives the acetal of methylglyoxal. Methylglyoxal is obtained from the acetal by hydrolysis with dilute sulphuric acid.

$$CH(OEt)_2{\cdot}CO{\cdot}CH_2{\cdot}CO_2Et \rightarrow CH(OEt)_2{\cdot}CO{\cdot}CH_3 \rightarrow COH{\cdot}CO{\cdot}CH_3.$$

Ethyl γ-diethoxyacetoacetate readily yields mono- and di-alkyl derivatives on successive treatment with sodium and alkyl haloids, thus furnishing a convenient method for the preparation of new substituted γ-diethoxyacetoacetic esters, alkyglyoxals, and their corresponding acetals. The following substances have been prepared:—

Ethyl γ-diethoxy-α-methylacetoacetate, *ethylgloxal* and its acetal; *ethyl γ-diethoxy-αα-dimethylacetoacetate*, *isopropylgloxal* and its acetal; *ethyl γ-diethoxy-α-methyl-α-ethylacetoacetate*, sec.-*butylglyoxal* and its acetal; *ethyl γ-diethoxy-α-*iso*propylacetoacetate*; iso*butylglyoxal* and its acetal; *ethyl γ-diethoxy α-benzylacetoacetate*, *phenylethylgloxal* and its acetal.

The reactions of ethyl γ-diethoxyacetoacetate are still under investigation.

98. "*The Action of Sulphuric Acid on Paraformaldehyde.*" By JOHN GUNNING MOORE DUNLOP.

When paraformaldehyde is heated for twenty-four hours in a sealed tube with a little sulphuric acid at 115—120°, the contents are converted into a liquid, which on distillation gives two fractions. One of these is methyl formate, and the other, which boils at 90—100°, is found to contain hydroxymethyl ether, $CH_3.O.CH_2.OH$, and somewhat indefinite compounds of the type—

$$CH_3{\cdot}O[CH_2O]_2{\cdot}CH_2{\cdot}OH$$

(compare Reychler, *Bull. Soc. Chim.*, 1907, [iv], i., 1189).

Since the paraformaldehyde was shown to be free from methyl alcohol, the latter must have resulted from the decomposition of the methyl formate, which in turn is derived from the condensation of two molecules of formaldehyde.

99. "*The Destructive Distillation of Soil.*" (Preliminary Note.) By ERIC JOHN HOLMYARD.

With a view to obtain further insight into the nature of the organic matter in soil, various soils have been destructively distilled from an iron retort. At a temperature of low redness, a distillate of two layers was obtained; the lower, aqueous, layer was strongly alkaline, and smelt of ammonia. The upper layer consisted of small quantities of a brown oil, possessing a characteristic odour resembling that of pyridine. Qualitative tests on the aqueous layer showed the presence of phenol and ammonia. The oil, after the addition of alkali, was purified by distillation in a current of steam, and was then pale yellow. On exposure to air for some days it darkened. Qualitative tests indicated the presence in it of pyridine, quinoline, pyrrole, indole, thiophen, and possibly furfuraldehyde.

Both field soils and garden soils give similar results, although the yield of oil was greater in the case of the garden soils.

The results are consistent with the view that the processes of decomposition occurring in the organic matter in soil are similar to those operative in the formation of coal. Further experiments on the subject are in progress.

100. "*Dibenzoylglucoxylose, a Natural Benzoyl Derivative of a New Disaccharide.*" By FREDERICK BELDING POWER and ARTHUR HENRY SALWAY.

The crystalline compound *dibenzoylglucoxylose* (m. p. 147—148°), $C_{11}H_{18}O_{10}(CO{\cdot}C_6H_5)_2,H_2O$, which represents the bitter constituent of the leaves and stems of *Daviesia latifolia*, R. Br. (*Trans.*, 1914, cv., 772), has now been completely examined with respect to its properties, and those of the disaccharide (*glucoxylose*) which it yields by its primary hydrolysis.

101. "*The Molecular Weights of some Salts of the Alkali Metals and an Account of the Compounds of these Salts with the Alcohols.*" By William Ernest Stephen Turner and Crellyn Colgrave Bissett.

The results of an investigation (shortly to be published) on the influence of the solvent on the molecular weights of salts (Turner and Pollard) have been applied to interpret the behaviour in solution of the salts of the alkali metals, more particularly those with the halogen elements, and it was argued that the non-associated state of these salts found by several previous workers could be satisfactorily accounted for by the influence either of the dielectric character of the solvent or of the temperature of the determination.

In the series of alcohols—ethyl, *iso*butyl and *iso*amyl—it was demonstrated that the molecular weights of lithium chloride, bromide, iodide, and nitrate rise as the dielectric constant of the solvent falls. The complication arising through the combination of solvent and solute was discussed, and the five possible types of behaviour owing to concurrent association and chemical combination were illustrated. Association is most pronounced with lithium nitrate, which does not enter into combination with the solvents employed. The associated character of the lithium salts was demonstrated further by molecular-weight determinations in acetic acid.

The lithium haloids combine with the alcohols to form compounds $LiCl(Br,I),3MeOH$ and $LiCl(Br,I),4ROH$, where R may be the ethyl, *n*-propyl, *iso*butyl, or *iso*amyl radicle. The compounds $NaI,3MeOH$ and $NaI,3CH_3{\cdot}CO_2H$ were also isolated.

102. "*Consistent Molecular Formulæ.*" By William Ernest Stephen Turner.

From the point of view of Avogadro's hypothesis, it was argued that many of the common molecular formulæ still in use, such, for example, as H_2, I_2, P_4, $SnCl_2$, and $C_2H_4O_2$, cannot be regarded as derived consistently, nor can they, as the outcome of modern work, be considered as adequate.

When molecular weights are derived from measurements in solution, an additional factor is introduced in the effect of the solvent, rendering a complete comparison with vapour-density determinations impossible. The conditions to be observed in order to make the comparison as favourable as possible were discussed.

It was argued that the molecular weight of a substance is, in most cases at any rate, a property dependent on temperature, pressure, and the medium, just as any other physical property, and that, in consequence, the only satisfactory mode of writing molecular formulæ is by a formula X_n, in the case of elements, or $(XY)_n$ for compounds, where n is to be given the value which holds for the particular conditions of existence.

For some substances, n remains constant over a wide range. Thus, for hydrogen, $n=2$ over a wide range of conditions, but at a very high temperature may become 1. For sulphur, this variation extends from $n=8$ to $n=1$.

The use of molecular formulæ in the way advocated would emphasise the connexion between the chemical and physical properties and the molecular weight.

103. "*Note on the Formation of Triphenylcarbinol.*" By Maurice Copisarow.

Friedel and Crafts (*Comptes Rendus*, 1877, lxxxiv., 1452; *Ann. Chim. Phys.*, 1884, [vi], 1, 500) found that on distilling the condensation product obtained from carbon tetrachloride and benzene in the presence of aluminium chloride triphenylmethane was chiefly produced, along with some triphenylcarbinol and possibly tetraphenylmethane.

E. and O. Fischer (*Annalen*, 1878, cxciv., 254), repeating Friedel and Crafts' experiment in the same manner, obtained chiefly triphenylmethane and a little triphenylcarbinol, but failed to detect any tetraphenylmethane.

Hinsberg (*Ber.*, 1899, xxxii., 2422), replacing aluminium chloride by ferric chloride in the condensation of carbon tetrachloride with benzene, found the product, on distillation in a current of steam, to consist of triphenylcarbinol only.

The question arises whether the difference in the products is due to the dissimilar experimental conditions or to the different effect of the metallic chlorides. In order to decide this, the author has performed the following experiments:—

(1) Sixteen grms. (1 mol.) of carbon tetrachloride were mixed with 25—30 grms. (3—4 mols.) of benzene, and 250 cc. of carbon disulphide added; 45 grms. of aluminium chloride were gradually introduced, the reaction being allowed to cease after each portion before further addition. The mixture was heated on the steam-bath for about nine hours, and afterwards decomposed with ice and hydrochloric acid, the carbon disulphide removed, and the product subjected to distillation with steam. The residue, a dark solid mass, was dissolved in alcohol, from which triphenylcarbinol crystallised; the latter was dissolved in benzene, the solution boiled with animal charcoal, and filtered, when, on cooling, large, white, rhombic crystals of triphenylcarbinol, melting at 159°, were obtained. The yield was 19 grms.

(2) Hinsberg's experiment (*loc. cit.*) was repeated, but the product was submitted to distillation as described by Friedel and Crafts. The product was found to consist chiefly of triphenylmethane (m. p. 92°) and a small amount of triphenylcarbinol.

From these experiments the conclusion may be drawn that aluminium chloride is identical in its effect with ferric chloride, but being more energetic it is to be preferred, as it gives better yields and requires less time to complete the reaction.

The real difficulty in obtaining very good yields is in the large amount of tarry matter formed during the reaction.

The difference in the products obtained by Friedel and Crafts and E. and O. Fischer on the one hand, and by Hinsberg on the other, is due to the secondary effect during the distillation without steam in the former case.

No tetraphenylmethane was detected in the author's experiments.

104. "*The Ionisation of Acids and their Activity as Catalysts.*" By Harry Medforth Dawson.

Recent experiments (Dawson and Powis, *Trans.*, 1913, ciii., 2135) have shown that the rate of isomeric change of acetone in dilute aqueous solution under the catalytic influence of acids can be represented by the equation $v=k_{H}c\alpha+k_{M}c(1-\alpha)$, in which v is the reaction velocity, c the concentration of the acid, α its degree of ionisation, and k_H and k_M are the activity-coefficients for the ionised and non-ionised acids respectively. For hydrochloric acid, the degree of ionisation employed in the calculation was that yielded by conductivity data, whilst for dichloroacetic, $\alpha\beta$-dibromopropionic, chloroacetic, and acetic acid the value of α was calculated from the ionisation-coefficient, $K=c\alpha^2/(1-\alpha)$.

According to Wegscheider (*Zeit. Phys. Chem.*, 1909, lxix., 603), the mass-action equation is no longer satisfied by the conductivity data if the ionic concentration exceeds a certain limiting value. Empirical formulæ connecting the degree of ionisation and the concentration have been suggested by Kraus and Bray (*Journ. Amer. Chem. Soc.*, 1913, xxxv., 1315) and by Kendall (*Trans.*, 1912, ci., 1275), which take into account the inter-ionic action which is supposed to give rise to the increase of $c\alpha^2/(1-\alpha)$ in solutions of higher concentration.

Assuming that the deviations from the mass law which are indicated by these empirical equations are true deviations, it is somewhat surprising to find such a close agreement between the observed and calculated reaction velocities when the value used for the degree of ionisation is that calculated on the basis of the mass law.

According to Kendall (*loc. cit.*, p. 1295), the ionisation of dichloroacetic acid can be represented by the formula

$c\beta^2/(1-\beta) = 0.0316 + 0.080(1-\beta)/\beta$, where β is the degree of ionisation at concentration c. If the values of β given by this formula are substituted in the equation $v = k_H c\beta + k_M c(1-\beta)$, the combination of the two extreme solutions ($c = 0.01$ and 0.2) gives $k_H = 462$ and $k_M = 126$, whereas the α values derived from the mass action formula yield $k_H = 445$ and $k_M = 203$. Both pairs of coefficients give almost equally good results in so far as the agreement between the observed and calculated velocities for acid solutions of intermediate concentration is concerned. This is shown in the following table, in which the first column gives the concentration of the acid, the second and third the values of α and β, the fourth and fifth the corresponding calculated velocities v_α and v_β, and the sixth the observed velocity, v.

Dichloroacetic Acid.

c.	α.	β.	v_α.	v_β.	v.
0·01	0·856	0·845	(4·10)	(4·10)	4·10
0·02	0·769	0·778	7·79	7·75	7·95
0·05	0·621	0·675	17·7	17·65	18·1
0·1	0·503	0·593	32·5	32·5	32·7
0·2	0·393	0·512	(59·6)	(59·6)	59·6

According to the results in this table, there is nothing to choose between α and β values for the degree of ionisation. It should be noted, however, that the reaction velocities under v_β are calculated on the basis of a coefficient $k_H = 462$, which deviates appreciably from the coefficient $k_H = 437$ derived from the data for hydrochloric acid. The divergence is greater than that shown by any one of the k_H values which are obtained from the data for the four weaker acids on the assumption that the ionisation occurs in accordance with the mass law. The agreement between the separate values of k_H (*loc. cit.*, p. 2142) is the more remarkable when the difference in the ionic concentration of the solutions used is taken into account.

From the above comparison, it is evident that the degree of ionisation of acids in relatively concentrated solutions must be determined with greater precision before it is possible to assign final values to the activity-coefficients of the non-ionised acids. Experiments with this object in view are in progress.

105. "*Synthesis of* dl-*Tyrosine and* dl-3 : 4-*Dihydroxyphenylalanine.*" By Henry Stephen and Charles Weizmann.

In continuation of previous work (*Proc.*, 1912, xxviii., 147), the authors have obtained the following new substances, in addition to those already mentioned in the above note :—

*Phthalamino-*p-*methoxybenzylmalonic acid*, obtained by hydrolysing ethyl phthalimino-*p*-methoxybenzylmalonate, is a white powder crystallising from acetic acid in plates, and melting and decomposing at 210°.

Phthalaminopiperonylmalonic acid, obtained from the corresponding condensation product, melts and decomposes at 234°. On hydrolysis with hydrochloric or hydrobromic acid, the *hydrochloride* (m. p. 246°) or *hydrobromide* (m. p. 212°) of 3 : 4-*dihydroxyphenylalanine* is obtained.

106. "*Optically Active Derivatives of* d-*Dimethoxy- and* d-*Diethoxysuccinic Acids.*" By Charles Robert Young.

The preparation of methyl *d*-diethoxysuccinate was described; the specific rotation of the pure liquid was found to be almost identical with that of the isomeric ethyl *d*-dimethoxysuccinate.

The optically active anilic acids, anils, anilides, and hydrazides derived from *d*-dimethyoxy- and *d*-diethoxysuccinic acids have been prepared, and their rotatory powers compared. No evidence of the formation of *iso*anils was obtained.

d-Dimethoxysuccinamic acid and the corresponding imide were also prepared, and the latter was converted into its methyl derivative by alkylation with silver oxide and methyl iodide.

107. "*Rate of Evolution of Gases from Supersaturated Solutions. Part II. Carbon Dioxide in Solutions of Gelatin and Starch.*" By Alexander Findlay and George King.

In continuation of the previous investigation (*Trans.*, 1913, ciii., 1170), it was shown that the rate of escape of carbon dioxide from solutions of gelatin and of starch is markedly affected, and more especially so in the case of dilute solutions, by the method of treatment of the solution. The shorter the time during which the solutions are boiled (to remove air), and the more rapid the cooling of the boiled solutions, the greater is the influence of the colloidal solution on the rate of escape of gas. The results obtained, more especially in the case of solutions of gelatin, lead to the conclusion that the difference in the behaviour of such solutions, as compared with water, is due, mainly, to the concentration of the gelatin *sol*, and not to the presence of the gel.

108. "*The Oxidation of Carbohydrates and Related Substances by means of Potassium Persulphate.*" By John Kerfoot Wood and Nellie Walker.

The authors have made a comparative study of the rates of oxidation of a number of carbohydrates and kindred substances by potassium persulphate in the presence of silver sulphate. In the absence of the silver salt the reaction proceeds very slowly, but the addition of small quantities of a 0·5 per cent solution of silver sulphate produces a marked acceleration of the process of oxidation. The experiments were conducted at 25°, and the solution of persulphate was almost saturated at that temperature. Equivalent amounts of the carbohydrates were employed, and sufficient of the persulphate solution to supply 1 atom of oxygen per molecule of carbohydrate was added. (With disaccharides, 1 atom of available oxygen per half molecule of sugar was added). The reaction was followed by removing portions of the mixtures from time to time, and measuring the acidity of the solution. Velocity-constants were calculated by means of the bimolecular formula. The results show that galactose, arabinose, and xylose are all oxidised at about the same rate; the velocity of oxidation of dextrose is slightly lower than in the case of the three sugars mentioned, whilst the rate for rhamnose is a little lower than that for dextrose. The authors consider that in the case of these five sugars it is extremely probable that under the conditions employed the sugars are almost quantitatively converted into the corresponding aldonic acids.

The velocity of oxidation of lævulose is greater than that of dextrose, and the process does not appear to be of so simple a character.

The disaccharides are oxidised more rapidly than the simple sugars.

With the polyhydric alcohols it was impossible to obtain, in the majority of cases, a definite velocity-constant. This indicates the occurrence of secondary reactions, the alcohol probably being partly converted into an aldehyde, which is then more rapidly oxidised than was the original substance.

109. "*Allanturic Acid.*" By Arthur Walsh Titherley and Noel Guilbert Stevenson Coppin.

The syrup described as allanturic acid in the literature, obtained by the decomposition of allantoin by hot aqueous nitric acid and by other means, has been shown by the authors to be a mixture the composition of which is dependent on its origin, the essential constituents being carbamidoglycollic acid, $NH_2{\cdot}CO{\cdot}NH{\cdot}CH(OH){\cdot}CO_2H$, its lactam, glyoxalylcarbamide, $\begin{array}{l}CO{-}{-}{-}NH\\ |\\ CH(OH){\cdot}NH\end{array}\!\!>\!CO$, and a very weak base, $C_3H_5O_2N_3$, may also be present.

The syrup obtained from allantoin and nitric acid by Pelouze, and later by Mulder, has been closely studied. On treatment with acetone, it falls to a white powder containing about 60 per cent of glyoxalylcarbamide, the remainder being chiefly the compound $C_3H_5O_2N_3$, partly

present as nitrate. Since the latter dissociates on dissolving in water, giving free nitric acid, the powder appears to possess pronounced acid properties, but the glyoxalylcarbamide component is itself only a pseudo-acid requiring about 40 per cent of an equivalent of alkali to show a neutral point (indefinite) to phenolphthalein in dilute aqueous solution. The "glyoxalylcarbamide" of Medicus cannot, on account of its properties and mode of formation be this lactam, and the present investigation throws no light on its nature.

Evidence bearing on the nature of "allanturic acid" has been obtained by a study of the decomposition of allantoic acid by nitric acid under varying conditions. At 0° or 15° with concentrated nitric acid, 1 molecule of carbamide is eliminated, and after concentration in a vacuum in the cold, a syrup or amorphous solid is obtained, consisting of glyoxalylcarbamide and the nitrate of a carboxylic acid, probably carbamidoglycollic acid,—

$$NH_2{\cdot}CO{\cdot}NH{\cdot}CH(OH){\cdot}CO_2H.$$

With aqueous nitric acid at 100° the decomposition is complete in a few minutes, but less than 1 molecule of carbamide is split off, and ammonia is eliminated. On now (1) concentrating in a vacuum and treating the syrup with acetone, impure glyoxalylcarbamide is obtained in small yield, but on (2) concentrating at 100° carbon dioxide is eliminated, and the syrup with acetone gives a relatively large yield of glyoxalylcarbamide admixed with the nitrate of the base, $C_3H_5O_2N_3$. These facts indicate that the allantoic acid decomposes in two ways, namely, (*a*) by hydrolysis, yielding carbamide and carbamidoglycollic acid, which during concentration suffers incomplete conversion into glyoxalylcarbamide; (*b*) by elimination of ammonia, yielding 4 : 6-diketohexahydro-1 : 3 : 5-triazine-2-carboxylic acid, which at 100° in the presence of nitric acid loses carbon dioxide, and furnishes 4 : 6-diketohexahydro-1 : 3 : 5-triazine (the weak base $C_3H_5O_2N_3$).

110. "*The Reaction between Sodium Benzylthiosulphate and Iodine.*" By THOMAS SLATER PRICE and ARTHUR JAQUES.

The velocity of the reaction between sodium benzylthiosulphate and iodine in potassium iodide solution, which takes place according to the equation :—

$$2NaO{\cdot}SO_2{\cdot}S{\cdot}CH_2{\cdot}C_6H_5+2H_2O+I_2= \\ =(C_6H_5{\cdot}CH_2)_2S_2+2HI+2NaHSO_4,$$

has been investigated in aqueous solution at 25°. Experiments with either component in excess showed that the reaction is unimolecular, both with respect to the sodium benzylthiosulphate and with respect to the free iodine; apparently the tri-iodide ion does not enter into reaction. When the components are present in equivalent concentrations, the velocity-constants are satisfactory in the more concentrated solutions, but rise continuously in the more dilute solutions; moreover, the value of the constants varies in the different solutions. The rise and variation in the constants were discussed and shown to be due, in all probability, (1) to the catalytic influence of the precipitated benzyl sulphide, owing to adsorption of iodine; (2) to the fact that the anion of the sodium benzylthiosulphate is alone concerned in the reaction.

The first stage in the reaction is probably the combination of a molecule of sodium benzylthiosulphate with one of iodine, in accordance with the equation :—

$$C_6H_5{\cdot}CH_2{\cdot}S{\cdot}SO_2{\cdot}ONa+I_2=C_6H_5{\cdot}CH_2{\cdot}SI_2{\cdot}SO_2{\cdot}ONa.$$

The compound thus produced is then decomposed very quickly, with the formation of benzyl disulphide, sodium hydrogen sulphate, and hydriodic acid.

111. "*The Dynamics of the Action of Halogens on Aliphatic Aldehydes. Keto-enol Isomerism of the Aldehydes.*" By HARRY MEDFORTH DAWSON, DONALD BURTON, and HARRY ARK.

Kinetic experiments relating to the action of bromine and iodine on acetaldehyde and its homologues have been made in dilute aqueous (or aqueous-alcoholic) solution, in which the rate of disappearance of the halogen was measured. The majority of the observations were made with acetaldehyde, and in all cases the aldehyde was present in relatively large quantity compared with the halogen.

The results obtained indicate that oxidation and substitution may both occur in the action of bromine on the aldehydes in dilute aqueous solution. Whereas in neutral solution the whole of the bromine is used up in the oxidation of the aldehyde, substitution takes place simultaneously if the solution is rendered strongly acid by the addition of a mineral acid. The relation between the quantities of bromine, which are used up in oxidation and substitution respectively, depends on the concentration of the free bromine and on the acidity of the solution. In a N-hydrobromic acid solution the concentration of free bromine is only about one-twentieth of the total bromine-concentration as a consequence of the formation of polybromide (HBr_3), and in these circumstances it was found that the substitution reaction is the predominant reaction, whereas oxidation is predominant in a N-hydrochloric acid, and still more so in a N-sulphuric acid solution.

In neutral solution, iodine reacts with acetaldehyde very slowly, but the rate of disappearance of the halogen is greatly increased in the presence of a mineral acid. The reaction velocity in acid solution is nearly constant, and the velocity-coefficient is practically identical with the coefficient calculated for the substitution reaction from the data obtained in the experiments with bromine.

The experimental facts suggest that halogen substitution in the aldehydes is conditioned by preliminary isomeric transformation of the aldehyde from the ketonic to the enolic form, the velocity of this change being greatly increased in the presence of acids.

112. "*Equilibrium in the System : Ethyl Alcohol, Acetic Acid, Ethyl Acetate and Water, and its Apparent Displacement by Mineral Chlorides.*" By JAMES FLETCHER and WILLIAM JACOB JONES.

It has already been shown (*Trans.*, 1911, xcix., 1427) that hydrogen chloride disturbs the above equilibrium owing to the formation of hydrate. In the present investigation these observations have been extended so as to include lithium and calcium chlorides.

113. "*The Mechanism of Cyanidion Catalyses.*" By WILLIAM JACOB JONES.

A chemico-dynamical investigation of the interaction between hydrogen cyanide and certain organic anions containing a double bond was described. It was shown that the speed of addition was proportional to the concentration of cyanidion present.

114. "*The Interaction between Hydrogen Cyanide and Aldehydes and Ketones in Dilute Solution.*" By WILLIAM JACOB JONES.

It was shown that in dilute solution equilibria of the type $RR'CO+HCN \rightleftarrows RR'C(OH){\cdot}CN$ are established. Water and, to a less extent, alcohol exert a dissociative influence on cyanohydrins.

Oxalacetic Acid.—H. Gault.—Oxalacetic ether is very readily prepared by the condensation of oxalic ether with acetic ether in presence of sodium or sodium ethylate. When distilled it is not stable, but alters more or less rapidly even at the ordinary temperature, undergoing progressive lactonisation. Under the action of heat the proportion of lactone formed amounts to 70—80 per cent at 150°. Hence it is necessary to avoid overheating during distillation. It also lactonises when left in contact with dilute solutions of potassium carbonate or bicarbonate. Oxalacetic ether has characteristic acid properties, readily yielding, for example, the corresponding potassium salt with concentrated solutions of potassium carbonate or bicarbonate.—*Comptes Rendus*, clviii., No. 10.

NOTICES OF BOOKS.

Indiarubber Laboratory Practice. By W. A. Caspari, B.Sc. (Vict.), Ph.D. (Jena), F.I.C. London: Macmillan and Co., Ltd. 1914.

As representing the results of the author's ten-year-long experience of rubber analysis this little book has a certain value. It does not aspire to be an exhaustive or critical treatise, but rather to be a strictly practical manual in which the chemist engaged in rubber analysis may find some useful hints. In it the analysis of crude and of manufactured rubbers are treated fairly fully, and the apparatus used for the various experiments is described and illustrated. No theoretical questions are discussed, and mechanical methods of testing are not included. On the whole, the book seems likely to serve its purpose, and chemists who have had a good general training in analytical work will with its aid be able to cope with the special case of rubber analysis.

The Pigments and Mediums of the Old Masters. By A. P. Laurie, M.A., D.Sc. London: Macmillan and Co., Ltd. 1914.

The object of the investigations described in this book was to obtain definite information as to the different pigments and mediums used at various dates, by means of which information the dates of works of art could be fixed and forgeries detected. For this purpose the author had to devise some special pieces of apparatus for the removal and examination of microscopical samples. After dealing with the properties and reactions of certain pigments which are of importance in the history of art he passes to the description and identification of the pigments used in the illuminated manuscripts of all nations, and applies the information thus obtained to the examination of pictures, finally showing in tabular form the range in time of the use of the most important pigments, summarising the results from the year 800 to 1800. Mediums are then similarly treated, but possibly the most interesting part of the book is that devoted to the application of microphotography to the study of brush work. This is admirably illustrated by plates which are fully explained, and the author shows how, from a careful study of microphotographs, conclusions may be drawn as to the authenticity of pictures.

Some Fundamental Problems in Chemistry, Old and New. By E. H. Letts, D.Sc., &c. London: Constable and Co., Ltd. 1914.

The aim of the author of this book is to contrast old views of atoms and elements with modern conceptions of electrons, and for this purpose he first discusses the views of the ancients regarding the nature of matter, and also describes in detail the development of the atomic theory and the Periodic Law. Many numerical data are given relating to determinations of atomic weights, and much of the information in the first part of the book might be learned from the usual text-books; however, the author has a knack of interesting his reader in what might otherwise be regarded as rather dull details, and often puts forward his facts in a novel way, quoting largely from the original descriptions of discoveries. The second part, beginning with Chapter V., deals with the newer chemistry, and in this part the chief facts and theories of radio activity are discussed. The views and work of Lockyer in inorganic evolution, and of Arrhenius on the origin and decay of worlds, are admirably described, and many students will be glad to be able to get a summary of their truly epoch-making work. The author's treatment of his subject is essentially modern, and he is usually and, on the whole, well up-to date; he makes no mention, however, of recent work on the nature of X-radiation, nor does he allude to Sir J. J. Thomson's latest pronouncement regarding the unknown substance "X_3."

The Russian Year-book for 1914. Compiled and Edited by Howard P. Kennard, M.D., Assisted by Nellie Peacock. London: Eyre and Spottiswoode, Ltd.

This year-book is invaluable for all who are interested in the resources and activities of the Russian Empire, and contains much general information which will be useful to the intending visitor. Many new diagrams have been added, and the statistics have in all cases been brought down to date. An interesting section on Russian literature is now included, giving a short account of its development and chief features.

The Carnegie Trust for the Universities of Scotland. Twelfth Annual Report (for the year 1912-13). Edinburgh: The University Press. 1914.

The twelfth annual report of the Carnegie Trustees is somewhat more detailed than previous reports, giving a general account of the operations of the trust during the past five years. The report clearly shows how greatly the Trust has fostered and encouraged a spirit of research among University students and others, and testifies to the continued success of the scheme. The main features of the plan of endowment of post graduate study and research are outlined, and annotated lists are given of the published works of beneficiaries.

Annual Report of the Board of Scientific Advice for India for the Year 1912-13. Calcutta: Superintendent Government Printing Office. 1914.

The chemical work done in the laboratory of the Industrial Section of the Indian Museum at Calcutta during the year 1912-13 was connected almost entirely with the investigation of substances of vegetable origin, fixed volatile oils, tanning materials, drugs, &c. In the agricultural section an important research on the gases of swamp rice soils was begun, and valuable work was done on the date sugar palm. The reports upon the work in geology, botany, zoology, &c., are included in the volume, as well as a short account of the scientific and technical investigations conducted for India at the Imperial Institute during the year ending June 30, 1913.

Bulletin of Armour Institute of Technology, Chicago. Vol. vii., No. 1. Chicago: Armour Institute of Technology Press. 1913.

This general information number of the Armour Institute of Technology contains detailed syllabuses of the courses of study at the Institute in the various departments. A complete register of graduates and students, and information relating to fees, scholarships, and prizes are also included. The four-year courses in Mechanical Engineering, Electrical Engineering, Chemical Engineering, &c., appear to provide a well-balanced system of study, and the Institute is doing a useful work in providing all classes of students with opportunities of obtaining a thoroughly scientific technical education.

Albin Haller. By Ernest Lebon. Paris: Gauthier-Villars. 1913.

This book is one of the series "Savants du Jour" edited by M. Lebon, and contains an interesting biography of the famous chemist and a vivid picture of his striking personality. The chief publications of M. Haller, whose scientific activity has been remarkable, are briefly summarised. His articles dealing with organic and physical chemistry are grouped together according to subjects—camphors, phthaleins, alcoholysis, &c.—and an analysis is given of their main features, while a *résumé* is also given of each separate article of importance, with full references to the periodicals in which it is to be found. The whole is excellently arranged, and the editor has had M. Haller's own assistance in classifying the papers and reading the proofs.

Principes et Applications de l'Electrochimie. ("Principles and Applications of Electrochemistry"). By O. DONY-HÉNAULT, H. GALL, and PH. A. GUYE. Paris and Liége: Ch. Béranger. 1914.

THIS comprehensive treatise on electrochemistry is divided into three parts. In the first part the fundamental laws of the science are discussed, the phenomena of osmosis being first thoroughly explained. A clear treatment of the ionic hypothesis and electrolytic dissociation is to be found in this first section. In Part II. the technical applications of electrochemistry are described, including the electrolysis of water, of solutions of halogen and other salts, and of fused salts. The authors have been particularly careful to give a fair view of the electrochemical industry as it stands at present, while pointing out its potentialities and the possibilities of its extension in many directions. Only a very limited amount of space has been given to electro-metallurgical processes, those relating to the manufacture of copper being the only ones which are treated in detail. A chapter is devoted to the electric furnace and products obtained with it, and this forms an introduction to the last section, which consists of an excellent account of the electrical combustion of nitrogen, written by M. Ph. Guye, who has done much pioneer work in the subject.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Berichte der Deutschen Chemischen Gesellschaft,
Vol. xlvii., No. 4, 1914.

Action of Alkaline Reducing Agents on Disulphoxides and Sulphoxides. — A. Gutmann. — When sodium arsenite acts on disulphoxides the latter give up an atom of oxygen, and sulphinates and mercaptans are formed. This behaviour is a further proof of the fact that the two oxygen atoms in the disulphoxides, $R_2S_2O_2$, differ in their power of reacting. The reaction with potassium cyanide-potassium sulphide is similar. Sulphoxides give no reaction with these alkaline reducing agents.

Hydrofluoric Acid and Fluorsulphonic Acid.—Otto Ruff and Hans Julius Braun.—In the preparation of aqueous hydrofluoric acid from fluorspar and sulphuric acid it is best to use about 90 per cent sulphuric acid. If 95 to 100 per cent is used a yield of about 60 per cent of 95 to 96 per cent HF can be obtained, but not anhydrous acid. In the residues some calcium fluorsulphonate is found besides calcium sulphate and unchanged calcium fluoride. From fuming sulphuric acid and fluorspar fluorsulphonic acid can be obtained, the yields being greater the greater the amount of anhydride in the acid. An acid with 60 per cent of anhydride gives nearly the theoretical yield.

Fluorsulphonic Acid.—Otto Ruff.—Sodium fluorsulphonate can be prepared by heating together sodium chloride and fluorsulphonic acid, and extracting the unchanged chloride by means of alcohol. Fluorsulphonic acid is very stable when the temperature is raised, and even at 900° it does not undergo decomposition. At its boiling-point it can be decomposed by sulphur, giving sulphur dioxide and hydrofluoric acid. The author has investigated the red gas formed on heating potassium bichromate with calcium fluoride and sulphuric acid, but has come to no definite conclusions as to its nature. When potassium permanganate and fluorsulphonic acid are gently warmed together a violet gas is evolved, which explodes when shaken or warmed. It is uncertain whether it contains fluorine as an essential constituent or whether it is simply manganese heptoxide.

Higher Manganese Phosphides.—S. Hilpert and Th. Dieckmann.—When manganese is heated with red phosphorus, first to 400° for forty-eight hours and then to 600° for the same time in a sealed exhausted tube, the compound MnP_2 is formed. If this substance is cautiously heated in a current of hydrogen phosphorus distils over, and when the weight is constant the residue consists of the phosphide, MnP. Both these phosphides are ferromagnetic.

Atti della Reale Accademia dei Lincei.
Vol. xxiii. [i.], No. 3, 1914.

Chemical Action of Light. Auto-oxidations.—Giacomo Ciamician and P. Silber.—When a solution of acetic acid was exposed to the action of light for seven months it slowly underwent auto-oxidation and formic acid was formed. Glycollic acid in the same conditions was completely auto-oxidised, the products being carbon dioxide and formaldehyde. Malonic acid is only very little affected by oxygen in the light, while succinic acid is only partially oxidised. Saccharic acid undergoes auto-oxidation even in the dark. Cumarin polymerises, and oleic acid yields dioxy-stearic acid and nonyl and azelaic acids, besides other products. In the dark in presence of oxygen oleic acid only acquires a faintly acid reaction.

MISCELLANEOUS.

Royal Institution.—On Tuesday next, May 5, at 3 o'clock, Prof. W. Bateson will deliver the first of two lectures at the Royal Institution on (1) "Double Flowers"; (2) "The Present State of Evolutionary Theory"; and on Saturday, May 9, Prof. C. J. Patten, of Sheffield University, will begin a course of two lectures on "Bird Migration." The Friday Evening Discourse on May 8 will be delivered by Prof. Karl Pearson on "Albinism in Men and Dogs," and on May 15 by Prof. Frederick Keeble on "Plant Animals: A Study in Symbiosis."

Institute of Chemistry.—*Past List: March* (1914) *Examinations.*—Of ten candidates who presented themselves for the Intermediate Examination, nine passed:—A. S. Carlos, B.Sc. (Lond.); C. G. Collins; Miss Gwen Dyer, Nat. Sci. Tripos (Cantab.); F. L. Elliott; H. S. Foster; J. J. Geake; G. Harding; J. W. Sewill, B.A. (Cantab.); and G. T. Shipston. Of fourteen candidates who presented themselves for the Final Examination, eight passed. In the Branch of Organic Chemistry—P. K. Dutt M.A., B.Sc. (Calcutta); J. W. Harris, B.Sc. (Lond.), and E. Mather, B.Sc. (Lond.). In the Branch of th; Chemistry (and Microscopy) of Food and Drugs, Fertilisere and Feeding Stuffs, Soils and Water—P. S. Arup; C. Ws McHugo; F. S. Thurston, B.Sc. (Lond.); J. A. F. Wilkinson, B.Sc. (Lond.); and F. Wright, B.Sc. (Leeds).

Feed Water Difficulties.—"The problem of suitable feed water, although less serious in New England than in other parts of the country, is still a trouble maker in many plants. The formation of scale and the softening of water are due to the simplest of chemical reactions, and by an analysis of the water a competent chemist can readily predict in advance the proper amounts of suitable chemicals necessary to prevent scale or corrosion, and not only save the company the expense of frequent boring and replacing of tubes, but obviate the necessity of attempting to force heat through the same substance with which many of your steam-lines are insulated. The service of a chemist," said Mr. Carl F. Woods, secretary of the firm of Arthur D. Little, Inc., of Boston, when recently speaking before a group of street railway operators, "would prevent the purchase of a special compound at $1000 a year which consisted of 97 per cent water and 3 per cent molasses, or obviate the necessity of purchasing a mixture of soda-ash, tannin, and water under a brand name at 8 cents a pound when the principal ingredient can be obtained for 1 cent a pound.

What Determines the Quality of Paper.—After discussing the fundamental properties of paper, such as thickness, strength, stretch, opacity, and other physical and chemical properties entering into the make-up of a sheet of paper, Mr. Arthur D. Little, who is eminently fitted to discuss these questions through his long connection with the paper industry and the wide nature of the consulting practice of the concern of which he is president, continues by saying:—"The number of factors which are concerned with the quality of paper in its multitudinous applications to special uses is so great as to prevent consideration or even enumeration of them all. A paper for wrapping hardware or a card for mounting silver jewellery may seem to possess every desirable property, and yet be worse than useless because of a trace of sulphur. A printing-paper may develop 'whiskers' or clog the type by mineral filler, a coated paper may pick or develop odour, a cigarette-paper may burn badly, a writing-paper may allow the ink to spread because the size has been converted into peptones by over-heating, a filter-paper may fail to hold a fine precipitate or unduly retard the passage of liquid, and so on. Enough has been said to suggest to consumers of paper the complexity of the problems involved in the determination of quality, the importance of paper testing, and the advantages to both maker and consumer of carefully considered and intelligently drawn specifications defining quality as a function of intended use."

Embryo Engineers hear a Lecture on Technical Reports.—"The first thing the Engineer must remember when he is retained is that he stands in a fiduciary relationship to his client. He is retained to furnish a report which is to give facts and data which will form the basis for decision as to the advisability of making an investment. The accuracy of these facts must therefore be unquestioned, and they must include all the available material. Moreover, since the report is usually addressed to non-technical people, the language must be clear and simple. The reader should be assumed to know nothing of the subject, and technical terms should be defined when used for the first time." The above remarks were made by Mr. Arthur D. Little, in a recent lecture before the Chemical Society of the Massachusetts Institute of Technology. A large audience greeted the speaker because of the long and varied experience which he has had in consulting practice as a chemist and engineer. Continuing, Mr. Little emphasised the fact that an engineer's success depends on his ability to influence other men, and that therefore the cultivation of good English was an absolute necessity. "The form of the report is extremely important. Although paper, type, and binding have nothing to do with the subject-matter, they influence the reader's opinion and should be carefully considered. The title-page should be attractive, and the table of contents should be very full. The report proper opens with a statement of the object and scope of the report, the general method of attack, and of obligations incurred in the preparation as to sources of material, &c. The body of the report is usually divided into sections, which are treated as separate units, with a summary after each, and a complete summary after the last one. Diagrams are advisable wherever possible, and at the conclusion an appendix is placed, which contains all original material, results of analyses, photographs, personal letters, copies of newspaper clippings, &c., and a bibliography of the literature of the subject."

Printing and Allied Trades Exhibition.—This Exhibition, to be opened at the Royal Agricultural Hall by the Lord Mayor of London on May 13, 1914, promises to be of exceptional interest. It will be the largest and most representative Exhibition of its kind ever held in any part of the world, every available space in the Great Hall, the Gilbey Hall, King Edward's Hall, and the galleries being occupied with exhibits strictly appertaining to the graphic Arts; new machinery and appliances will be shown, alike interesting to the expert and the general public, in addition to a very fine display of specimens of printing by all processes, including photogravure. The Exhibition has the support and patronage of the various Societies associated with the Printing and Allied Trades, and practically every firm of repute in the industries represented is co-operating to make this quadrennial Exhibition an unqualified success. The Exhibition will remain open until May 30.

MEETINGS FOR THE WEEK.

Monday, 4th.—Royal Society of Arts, 8. (Cantor Lecture). "Some Recent Developments in the Ceramic Industry," by W. Burton, M.A.
— Royal Institution, 5. General Meeting.
— Society of Chemical Industry, 8. "Apparatus for the Automatic Measuring and Injection of Chemicals," by the Hon. R. C. Parsons. "Jets for Mixing," by O. Nagel. "A Reaction of Tetranitromethane," by W. R. Hodgkinson.

Tuesday, 5th.—Royal Institution, 3. "Double Flowers," by Prof. W. Bateson, F.R.S.

Wednesday, 6th.—Society of Public Analysts, 8. "Detection of Castor Oil Seeds," by G. D. Lander and J. J. Geake. "Composition of Milk," by H. D. Richmond. "Note on 'Sharps,'" by J. F. Liverseege and G. L. Elsdon. A Simple Form of Fat Extractor will be shown by G. A. Stokes.
— Royal Society of Arts, 8. "Inexpensive Motoring," by A. Ludlow Clayden.

Thursday, 7th.—Royal Institution, 3. "The Last Chapter of Greek Philosophy—Plotinus as Philosopher, Religious Teacher, and Mystic," by The Very Rev. W. R. Inge, D.D.
— Royal Society, 4. (Election of Fellows). "Some Calculations in Illustration of Fourier's Theorem," and "The Theory of Long Waves and Bores," by Lord Rayleigh. "Protection from Lightning and the Range of Protection afforded by Lightning Rods," by Sir Joseph Larmor and J. S. B. Larmor. "Flow in Metals subjected to Large Constant Stresses," by E. N. Da C. Andrade. "Properties of Magnetically-shielded Iron as affected by Temperature," by E. Wilson. "Eddy Motion in the Atmosphere," by G. I. Taylor.
— Royal Society of Arts, 4.30. "The Punjab Canal Colonies," by Sir James M. Douie, K.C.S.I.
— Chemical, 8.30. "Researches on Santalin," by J. C. Cain, J. L. Simonsen, and C. Smith. "Nature of Molecular Association—Its Relation to Chemical Combination," by W. E. S. Turner and S. English. "Action of Diastase on Starch Granules," by J. L. Baker and H. F. E. Hulton. "Studies in Substituted Quaternary Azonium Compounds containing an Asymmetric Nitrogen Atom—Part III., Resolution of Phenylmethylbenzylazonium Iodide into Optically Active Components," by B. K. Singh. "Contributions to the Chemistry of the Terpenes—Part XVII., The Action of Hypochlorous Acid on Camphene," by G. G. Henderson, J. M. Heilbron, and M. Howie. "Reactions by Trituration," by L. H. Parker. "Reaction between Dilute Acid Solvents and Soil Phosphates," by J. A. Prescott. "Influence of the Dilution of Hydrogen Peroxide on the Velocity of Precipitation of Manganese from Ammoniacal Solutions in presence of Zinc," by A. J. Walker and W. Farmer. "Quinone Ammonium Derivatives—Part III., Dihaloid-, Monoazo-, Bisazo-, Nitro-triazo-, Bistriazo, and Compounds containing an Asymmetric Quinquivalent Nitrogen Atom," by R. Meldola and W. F. Hollely. "Additive and Substitutive Derivatives of Mercuric Nitrite with Organic Thio-compounds," by P. C. Ray. "Co-ordination of Antimony Halides with Conjugated Compounds," by E. Vanstone. "Absorption Spectra of various Substances containing Two, Three, and Four Benzene Nuclei," by J. E. Purvis. "Kinetics of the Decomposition of Acyl Derivatives of Phenols by means of Alcohol in presence of Acids and Alkalis," by M. Jones and A. Lapworth.

Friday, 8th.—Royal Institution, 9. "Albinism in Men and Dogs" by Prof. Karl Pearson, F.R.S.
— Physical, 8. "Graphic Treatment of the Rainbow and Cusped Wave-fronts," by W. R. Bower. "Gyrostatic Devices for the Control of Moving Bodies," by J. G. Gray.

Saturday, 9th.—Royal Institution, 3. "Bird Migration," by Prof. C. J. Patten, M.A.
— Biochemical Society, 4. (In the Chemical Department, Royal Holloway College, Englefield Green, Surrey).

THE CHEMICAL NEWS.

Vol. CIX., No. 2841.

ON METALLIC COLLOIDS AND THEIR BACTERICIDAL PROPERTIES.*

THE HISTORY OF COLLOSOLS.

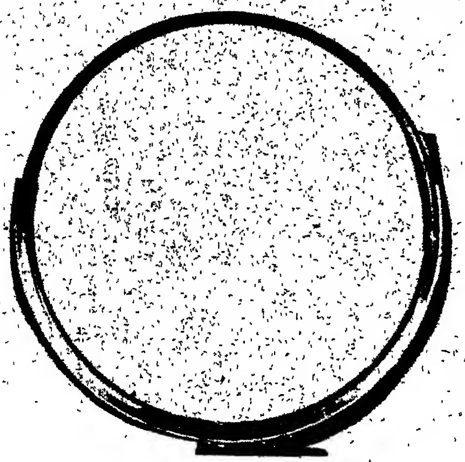
By HENRY CROOKES, F.C.S., A.R.S.M., M.I.E.E.

Man is always fighting against unseen foes. In the mediæval ages a question was often discussed, viz., "How many angels can stand on the point of a needle?" If instead of angels we say "devils" or "microbes,"—and devils are only angels of opposite polarity—the subject can be brought more clearly to our every day comprehension. Microbes of disease are the "devils" that medical science is always warring against; they are so small as to be invisible to the naked eye, and, in fact, can only be seen under a high power microscope—about 1000 can be placed on the point of a very fine needle. Modern science has, in spite of their minuteness, found them, identified them, photographed, isolated, cultivated, and finally devised means of killing them. The simplest method of killing microbes is by the application of heat; sunlight has also been found to be a very efficient sterilising agent. Various disinfectants, such as carbolic acid, chloride of lime, permanganate of potash, &c., have been proved to be deadly to microbes. Unfortunately for us human beings, nearly every efficient germicide known until recently has an irritating or destructive action on living organic tissues. The dream of the doctor has been to find an agent that will kill disease, or, in other words, bacteria, and will at the same time do no harm to the tissues of the human body. Immediately following the discovery of radium it was found that the emanations from that wonderful element had a very strong germicidal action, but almost at the same time it was noticed that a very serious burning effect on the skin and flesh was also produced.

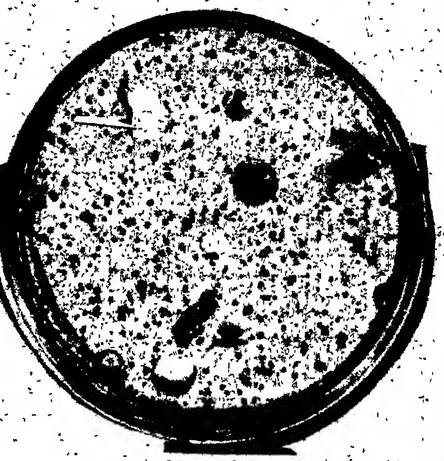
In June, 1903, I exhibited at the Royal Society a number of plate cultures and photographs, illustrating the germicidal action of radium emanations on several forms of microbes. The radium rays undoubtedly kill the microbes, but at the same time, unless administered with the most scrupulous care, they also kill, or *burn up*, the living tissues of the body.

The radium emanations are due to the breaking down of the atom of radium, and electrons are constantly flying off with about two-thirds the speed of light (182,000 miles per second). These electrons are now looked upon as being absolute units of negative electricity. To try and illustrate their size is difficult; imagine one drop of water magnified to the size of the earth (8000 miles diameter); an atom would then be about the size of a walnut or a cricket-ball. Now magnify the cricket-ball or atom to a cube of 100 ft. each side; the electron would be about the size of this dot (.) 1/100th of 1 in. diameter). The mind cannot conceive such figures.

About that time (1903), or shortly afterwards, the attention of medical men was directed in a critical scientific manner, apart from tradition and empiricism, to the curative effect of certain waters from mineral springs. Laborious research on the part of many workers has revealed the fact that these curative waters contain a number of extremely small metallic particles, endowed with continuous, rapid, oscillatory movement known as the "Brownian movement."



I.



II.

Photographs Illustrating the Preservative Effects of "Collosol Argentum."

Two plates of nutrient gelatin exposed on the window-sill for half-an-hour. No. I. had been covered previously with "Collosol Argentum" for five minutes, No. II. was untreated; both plates were incubated for forty-eight hours at 20° C. No. I. is sterile, No. II. contains about 350 microbes.—May 20, 1913.

This condition under which these particles are present is known as the "colloidal" condition. The word "colloidal" is really a misnomer, but it has gained currency by long use. The actual state in which these particles exist is that of extreme minuteness; they remain in suspension, being kept up by the continuous molecular bombardment of the surrounding liquid. Natural waters contain these metallic particles in comparative small numbers, and the problem arose how to increase the number and thus the efficiency of these particles in a solution. One method, known as Bredig's method, of effecting this result was by using a high tension disruptive electric spark under water, between poles of the metal to be dealt with. Solutions containing an almost incredible number of particles of metal were prepared by these means, and it was soon found that these liquids had a very high germicidal power. After a time it gradually became evident that these electric colloids, as the solutions were called, could not be depended upon; they were not stable and were

* Read before the Royal Society of Medicine, April 8, 1914.

broken down by the presence of electrolytes. The next problem was that of stabilising these colloidal solutions. As the workers increased in number the proposed methods multiplied. Organic compounds of metals were introduced, but all had drawbacks, such as non-stability, irritation, caustic effect, &c.

A few years later, during a research I was engaged in, I noticed a peculiar action of some metals in inhibiting the growth of bacteria in their neighbourhood; as a result of further work in following up this question I exhibited a number of living cultures and photographs of my experiments at the Royal Society and at the Royal Institution in May and June, 1911. The germicidal action of metals in these experiments is, at first sight, very similar to the observed germicidal action of radium, but with this enormous and important difference, that whereas radium kills and destroys the flesh as well as the bacteria, the other metals (in what is now called the colloidal state) kill the bacteria only, and exercise a bland and soothing effect on the animal tissues.

After further work on the subject, entailing about 2000 experiments, I was able to produce a harmless liquid containing metallic particles in suspension, endowed with the above described "Brownian" movement. I have called these preparations "Collosols." The germicidal action of colloid metals in suspension has been known for some time, especially during the last seven or eight years, in connection with medical and therapeutic work; but the great drawback in all previous preparations of this character, as has already been pointed out, is that—(1) They are not stable by themselves; (2) they break down instantly when introduced into a liquid containing even a small proportion of common salt, such as the blood (containing 0·7 per cent salt), and are therefore useless for the human body; (3) they are nearly all irritating to the animal tissues. "Collosols" have none of these drawbacks; they are permanently stable, they do not irritate the tissues, salt does not break them down, and they contain so small a proportion of metal, viz., 1 in 2000, that even a poisonous body like arsenic can be used with impunity. Well-known medical men have stated confidently that the dose is unlimited, as only the bacteria and ferments are killed.

Collosols can be applied topically as a lotion, by intramuscular or intravenous injections, or by the mouth, and from numerous trials made by a large number of medical men, as well as from very many laboratory experiments, it has been proved conclusively that there is no microbe that can withstand the action of collosols, when properly applied, for more than a few minutes.

Silver and Mercury "Collosols" of the normal strength (1 in 2000) were diluted with nine times the quantity of nutrient broth (1 in 20,000), and 10 cc. of this mixture were infected with two loopfuls of a vigorous culture of *B. coli communis*; after shaking, so as to mix thoroughly, streak cultures were made quickly on agar plates, the first within ten seconds, then at two, four, six, eight, and ten minute intervals. These plates were incubated at 37° C. for forty-eight hours, and gave the following results:—

Silver "Collosol" (1 in 20,000) with *B. coli communis*:—

After 10 seconds—Growth.
" 2 minutes "
" 4 " "
" 6 " No growth.
" 8 " "
" 10 " "

Mercury "Collosol" (1 in 20,000) with *B. coli communis*:—

After 10 seconds—Growth
" 2 minutes—No growth.
" 4 " "
" 6 " "
" 8 " "
" 10 " "

(In each case the blank or control streak gave a vigorous growth).

These experiments were repeated with silver and mercury "Collosols" at the normal strength of 1 part in 2000. In every case *B. coli communis was killed within ten seconds*, the only growth on the agar plates being those of the untreated control streaks. Several comparative tests were made with the *gonococcus* grown on agar plates smeared with fresh blood, with the usual precautions. A plate showing a vigorous growth and answering to the typical tests (that is—Gram-negative, no growth on gelatin or agar at 20° C. without fresh blood, but vigorous growth at 37° C. on agar with fresh blood, and displaying the well-known *diplococcus* in pus cells) was swamped with "Collosol" silver for two minutes, after which time streak cultures were taken and transplanted to agar plates smeared with fresh blood as before, at intervals of two, four, six, eight, and ten minutes, and incubated in the usual way at 37° C. *Result—No growth whatever.*

I have carried out many series of experiments similar to this; for instance, with a young vigorous growth of *B. tuberculosis*, I found that with "Collosol" Silver (1 in 2000) it was killed in four minutes. With *Staphylococcus pyogenes*, various *Streptococci*, and other pathogenic organisms, I find that all are killed in three or four minutes; in fact, *I know of no microbe that is not killed in laboratory experiments in six minutes.*

It will be argued that laboratory experiments are not of much value, because of the very different conditions in which bacteria exist in the human body; the answer to this objection is that with a safe bactericide, such as Collosols, of which the dose is unlimited, large quantities, such as one pint or more, can be injected intravenously (this has been done thousands of times with other liquids), and it is well known that a fluid injected into the body soon spreads throughout the whole system. In some circumstances it is desirable and even important to apply colloid metals, not only internally but locally, such as in the case of a diseased joint containing incapsulated bacteria (such as the *gonococcus* or *B. tuberculosis*). I have shown that this can be done by means of a very small electric current of about 30 to 40 milliampères with an E.M.F. of about 50 volts. Two blocks of solid nutrient gelatin were prepared, 2 ins. diameter and 1 in. thick. A current of 35 milliampères was passed through one of these (A) by means of silver pole plates 1¼ in. square, covered with flannel soaked in silver collosol; the current, obtained from a medical battery of 24 dry cells, was kept on for twenty minutes, the negative pole being placed on the top. The other block (B) was arranged in exactly the same manner, and left for twenty minutes, but no current was passed. Stab cultures of *B. coli communis* were made vertically through the centre of each block. Three days afterwards I noticed a growth along the line of the stabs, and in order to examine these more closely I made a vertical section of each block close to the stab. I then observed that in block (B) without current there was a vigorous growth of *B. coli* throughout the length of the stab, right up to the surface; whereas, in block (A) with current, there was no growth at the surface, nor for the top eighth of an inch, and below that only a feeble growth for the rest of the line of stab. This proves that the negative current of 35 milliampères had driven the colloidal particles of silver into the gelatin, where they were able to continue their germicidal activity, and that the particles did not soak into the gelatin to any appreciable extent, without the driving action of the electric current.

To show that medical electric currents do not break down collosols, I passed a current of 40 milliampères from the same 24 cells through 10 ozs. of Collosol Argentum contained in a glass vessel for one hour. The same silver pole plates 1¼ in. square were used, and were kept about 2 inches apart. After turning off the current the collosol was examined under the ultra-microscope, and it was observed that no change in the "Brownian" movement had taken place.

Much has been said as to the theory of this killing action. How is it brought about? With regard to the

radium emanations it is undoubtedly akin to burning; radium sores are in a way similar to burns but take very much longer to heal. Ultra-violet light, even at the temperature of liquid air (– 181° C.) has apparently a disruptive or bursting action. I show photographs illustrating this action.

It seems probable that the action of colloid metallic particles in killing bacteria is due to another cause. Assuming, as seems reasonable, and as has been definitely stated by some writers, that each metallic colloidal particle carries a charge of electricity, these particles in any definite preparation are all electrified in the same manner—negative, for example, in the case of silver—and are therefore mutually repelled, so that in spite of their constant and exceedingly active movement (about 6000 times their own diameter per second), they do not and cannot touch each other, and thus do not lose their charge. If, however, a foreign neutral body (such as a microbe) enters the solution, these electrified particles are not repelled from it automatically, but may even be attracted to it if it happens to carry a charge of the opposite polarity by the action of adsorption; in any case, being of much greater mass, the microbe will receive the charges of many thousands or millions of particles of metal, and this may very conceivably account for its death.

Bacteria are measured under the microscope in terms of μ (1/1000th of a millimetre), and the average size of a coccus may be taken as 1 μ diameter, or in the case of bacilli 1 μ in length. The size of colloidal metallic particles is, however, very much smaller, and they are measured in terms of $\mu\mu$ (1/1,000,000th of a millimetre). According to Zsigmondy, particles of more than 60 or 70 $\mu\mu$ in a liquid sink to the bottom, while those of less than 3 or 4 $\mu\mu$ cannot be seen under the ultramicroscope, even with bright sunlight as the illuminant. Thus the proportionate size of a microbe and the smallest visible metallic colloid particle is about 330 : 1, or to give a popular example, their relative sizes are as the elephant in the Natural History Museum compared with the shrew mouse underneath.

The number of colloidal particles in a liquid containing 0·05 grm. of gold per litre, or 0·005 per cent, is, according to Zsigmondy, 1,000,000,000 per cubic millimetre; assuming each particle to be 15 $\mu\mu$ diameter, owing to the difference in specific gravity, there would be about double the number of particles of silver. As Collosol Argentum contains 0·05 per cent—or ten times the amount of Zsigmondy's typical solution—the number of particles present would be, in round numbers—

$$1{,}000{,}000{,}000 \times 2 \times 10 \times 1000 \text{ per cc.} = 20{,}000{,}000{,}000{,}000 \text{ per cc. of 15 drops.}$$

An illustration of the protective value of "Collosols" is shown in two photographs (Figs. I. and II.). Two plates of nutrient gelatin peptone, A and B, were exposed on the window-sill for half-an-hour. A had been previously washed with Collosol Argentum, B was untreated. Both plates were then placed in the incubator at 20° C. for forty-eight hours. It will be seen that A is sterile, while B contains about 350 colonies of microbes. It must be admitted that about an equal number of bacteria in the dust will have fallen on the two plates during the time of exposure side by side; the result shows the *rôle* of colloidal metals in the form of "Collosols" as a protective agent in dressing wounds after operations, and also all smaller scratches, wounds, and sores on the body.

With reference to the medical employment of these preparations, my medical and other friends have, during the past two and a-half years, furnished me with very encouraging reports, which seem to warrant these remedies receiving a more extended trial by the medical profession.

(These preparations are manufactured by Crookes' Collosols, Ltd., and can be obtained at the Company's Laboratory, 109, Ladbroke Grove, London, W.).

SOME ERRORS IN THE DETERMINATION OF THE RARE EARTHS AS HYDROXIDES.

By T. O. SMITH and C. JAMES.

THE writers have observed that when the rare earths are precipitated as the hydroxides and ignited to oxides that the results are higher than when they are precipitated as oxalates and ignited. Moreover, the former method gives results which are not concordant with varying amounts of the precipitant. Since this method has been often recommended for quantitative determinations it seemed desirable that a careful investigation should be carried out.

As a basis for determining the source of error it was thought advisable to compare the following precipitants: Oxalic acid, ammonium oxalate, sodium hydroxide, and ammonium hydroxide. If the cause of error were due to the formation of a basic salt, lanthanum being the most powerful base of the rare earths would tend to give a maximum. It seemed preferable to use lanthanum chloride rather than lanthanum nitrate, since lanthanum hydroxide upon ignition would hold chlorine more readily than nitric acid.

A solution of pure lanthanum chloride was prepared by igniting a very pure lanthanum oxalate, dissolving the resulting oxide in a minimum amount of dilute hydrochloric acid, evaporating to dryness, and taking up in water. The solution was made faintly acid, by a few drops of hydrochloric acid, to convert any traces of basic chloride back to the normal salt.

Oxalic Acid.—Varying amounts of the lanthanum chloride solution were measured out, and precipitated in the cold by the addition of a slight excess of oxalic acid. The volumes in each case were kept constant so as to remove any doubt as to solubility. The precipitated solutions were allowed to stand over night. The oxalate was filtered off, washed with cold water, dried, and ignited. The results follow:—

No.	$LaCl_3$, cc.	Wt. of oxide.	Oxide, per cc.
1 ..	25	0·0866	0·003464
2 ..	25	0·0864	0·003456
3 ..	50	0·1729	0·003458
4 ..	50	0·1732	0·003464
5 ..	50	0·1729	0·003458
6 ..	75	0·2594	0·003459
7 ..	75	0·2596	0·003461
	Average		0·003460

Ammonium Oxalate.—In order to avoid the formation of free hydrochloric acid and consequent possible solubility of the oxalate during precipitation, ammonium oxalate was employed as reagent. The operations were identical with the above, except for the substitution of ammonium oxalate for oxalic acid. The results follow:—

No.	$LaCl_3$, cc.	Wt. of oxide.	Oxide. per cc.
1 ..	50	0·1725	0·003450
2 ..	50	0·1726	0·003452
3 ..	25	0·0864	0·003456
4 ..	25	0·0865	0·003460
5 ..	50	0·1729	0·003458
6 ..	50	0·1730	0·003460
7 ..	50	0·1728	0·003456
8 ..	75	0·2594	0·003459
9 ..	75	0·2592	0·003456
	Average (omitting 1 and 2) ..		0·003458

Sodium Hydroxide.—Varying amounts of the lanthanum chloride solution were taken, diluted, precipitated at the boiling-point, filtered, washed with hot water, dried, and gnited. The following figures were obtained:—

No.	$LaCl_3$, cc.	Wt. of oxide.	Oxide per cc.
1 ..	25	0·0878	0·003512
2 ..	50	0·1751	0·003502
3 ..	75	0·2619	0·003492
	Average		0·003502

The variation of these results with each other suggested precipitation with different amounts of the reagent. Three 50 cc. portions were taken, diluted, and precipitated at the boiling-point with a measured slight excess of sodium hydroxide solution. Three other 50 cc. portions were taken, diluted, heated to boiling, and precipitated with double the amount of sodium hydroxide. The data follow:—

No.	$LaCl_3$, cc.	Wt. of oxide.	Oxide, per cc.
1 ..	50	0·1751	0·003502
2 ..	50	0·1753	0·003506
3 ..	50	0·1755	0·003510
	Average		0·003506
4 ..	50	0·1772	0·003544
5 ..	50	0·1771	0·003542
6 ..	50	0·1768	0·003536
	Average		0·003541

Ammonium Hydroxide.—Varying amounts of the lanthanum chloride solution were taken, heated to boiling, precipitated with a slight excess of ammonium hydroxide, filtered, washed with hot water, dried, and ignited. The results follow:—

No.	$LaCl_3$, cc.	Wt. of oxide.	Oxide, per cc.
1 ..	25	0·0870	0·003480
2 ..	25	0·0871	0·003484
3 ..	50	0·1740	0·003480
4 ..	50	0·1742	0·003484
5 ..	75	0·2612	0·003483
6 ..	75	0·2616	0·003488
	Average		0·003483

When the results of the various precipitants are compared the following facts are brought out:—Ammonium oxalate gives figures similar to oxalic acid, with the exception that when an excess of ammonium oxalate is used the precipitate carries with it some ammonium oxalate. Upon washing the precipitate with water the complex ammonium lanthanum oxalate appears to undergo hydrolysis. When this takes place some lanthanum oxalate is produced in such a fine state of division that it passes through the filter-paper. The first two results among the ammonium oxalate determinations illustrate this fact. It was observed that these filtrates were somewhat opalescent.

The amounts of oxide are high when sodium hydroxide is used. This is evidently not due to the formation of a basic salt, since, when a large amount of sodium hydroxide is used, still higher results are obtained. The above facts indicate the carrying down of sodium. In order to prove the presence of sodium in the oxide it was dissolved in hydrochloric acid, and the solution tested for sodium by means of the flame coloration and the spectroscope. Both gave very decided tests for sodium.

Ammonium hydroxide was substituted for sodium hydroxide because of its volatile nature. But in this case also high results were obtained, although not as high as when sodium hydroxide was used. A qualitative analysis of the lanthanum hydroxide revealed traces of chloride which would indicate the formation of a certain amount of basic chloride. It is highly probable that ammonium hydroxide would give quantitative results if the lanthanum were present as the nitrate, because upon ignition the basic nitrate if formed would be readily broken down to oxide.

Durham, New Hampshire,
Feb. 24, 1914.

ANOMALOUS ROTATORY DISPERSION.*

By Prof. LEO TSCHUGAEFF, Royal University, St. Petersburg.

It has been well known since Biot's classical work on rotatory polarisation that most of the colourless active bodies exhibit "normal" rotatory dispersion, the numerical values of the optical rotation continuously increasing with decreasing wave-length (*cf.* H. Landolt, "Das Optische Drehungsvermögen," II. Aufl., Braunschw., 1898; P. Walden, *Berl. Ber.*, 1905, xxxviii., 345).

The dispersion ratios $\frac{[\alpha]_F}{[\alpha]_C}$ of compounds of this class vary for the most part within the limits 1·8 to 2·0. Quartz, cane-sugar, different active hydrocarbons, and alcohols may be cited as examples of such bodies.

Biot was also the first to point out that there are several exceptions to this rule, which belong to the domain of "anomalous" rotatory dispersion. This term is generally applied to those cases in which the optical rotation passes through a maximum or through a zero value, or decreases with decreasing wave-length. The rotation and dispersion of these substances are, however, largely influenced by the *temperature* and by the nature of the *solvent*, so that a substance which shows anomalous rotatory dispersion under some conditions may become normal under other conditions.

In the present state of our knowledge we can assume that all the cases of anomalous rotatory dispersion hitherto described may be divided into three classes.

1. To the first class belong all those cases in which anomalous dispersion is due to the *superposition* of the optical rotations of two (or more) *different kinds of normally dispersing molecules* differing in rotatory dispersion as well as in the sign of their rotation.

It was shown by Biot that dispersion of this kind may be observed in mixtures of dextro-rotatory camphor with lævo-rotatory oil of turpentine, and Arndsen put forward the supposition that the anomalous dispersion of tartaric acid is due to the same cause (*Ann. Chem. Phys.*, 1858, [3], liv., 858). Mixtures of *l*-menthone with isomenthone may be cited as a further example (L. Tschugaeff, *Zeit. Phys. Chem.*, 1911, lxxvi., 469).

2. Another type of anomalous rotatory dispersion is intimately related with the existence of *absorption bands* in the spectra of the active compounds in question. The discovery of this type is due to the French physicist, A. Cotton ("Recherches sur l'absorption et la Dispersion de la Lumière par les Milieux doués du Pouvoir Rotatoire," Thèse, Paris, 1896).

Cotton pointed out in 1896 that the dispersion curves of certain coloured solutions, containing, for example, double tartrates of copper or of chromium, go through a maximum in the next neighbourhood of the absorption band, the sign of the rotation being subsequently changed, and the curve going through a second maximum of the opposite sign.

Cotton has shown further that the anomalous dispersion in absorbing bodies is intimately allied with the so-called circular dichroism; that is to say, the two circular rays resulting from the original plane vibration are not equally absorbed by the active body.

It is well to mention here that Drude ("Optik," 1906), to whom we are indebted for a general electronic theory of dispersion, has shown that this theory is quite in accordance with Cotton's experimental results.

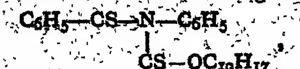
Cotton carried out his remarkable investigation with solutions of complicated composition; he was not able to isolate his active complex salts nor to obtain them in the state of purity. The same is true of the subsequent measurements of McDowell (*Physical Review*, 1905, p. 163) and of Grossmann (*Chem. Centrl.*, 1908, ii., 1996; *Zeit. Phys. Chem.*, 1910, lxxii., 93), who repeated and extended Cotton's experiments.

* A Contribution to a General Discussion on "Optical Rotatory Power," held before the Faraday Society, March 27, 1914.

Five years ago I discovered (*Berl. Ber.*, 1909, xlii., 2244) a series of coloured and active compounds showing anomalous rotatory dispersion of the same type as Cotton's double salts. These compounds were derivatives of the menthyl-, bornyl-, and fenchyl-xanthates and of the corresponding thiourethanes.

It was pointed out that there is a general parallelism between the absorption spectra of these bodies and the shape of their dispersion curves (L. Tschugaeff and A. Ogorodnikoff, *Zeit. Phys. Chem.*, 1910, lxxiv., 503; 1912, lxxix., 481). A still closer parallelism holds between the dispersion and absorption produced by one and the same active body in different solvents, the absorption and the dispersion curves being always displaced in the same direction by passing from one solvent (toluene) to another (acetone).

On the other hand, evidence was brought forward that the anomalous dispersion was not due to the influence of the solvent, since the compounds in question showed this property also in a state of superfusion (L. Tschugaeff and A. Ogorodnikoff, *Ann. Chim. Phys.*, 1911, [8], xxii., 137). But still more noteworthy is the recent work of Bruhat (*Comptes Rendus*, 1911, cliii., 248) and Cotton (*Comptes Rendus*, 1911, cliii., 245), who succeeded in observing circular dichroism in one of my substances—1 : 2-diphenyl-3-*l*-bornylimido xanthide—of the following constitution :—



and pointed out that the connection between this phenomenon and the sign of the optical rotation in both the antipodes is exactly the same as is required by theoretical considerations.

During the investigations performed in my laboratory it was shown that abnormalities may occur in the shape of the dispersion curve of an active and colourless compound if it exhibits an ultra-violet absorption band in the neighbourhood of the visible spectrum (L. Tschugaeff, *Zeit. Phys. Chem.*, 1911, lxxvi., 469; *Bull. Soc. Chim.*, 1912, [4], xi., 718; L. Tschugaeff and A. Kirpitcheff, *Bull. Soc. Chim.*, 1913, [4], xiii., 796).

Thus the dispersion ratio $\frac{[\alpha]_F}{[\alpha]_C}$ of many ketones goes far beyond the normal limits mentioned above, *e.g.* :—

Substance.	$\frac{[\alpha]_F}{[\alpha]_C}$	Solvent.
Camphor	2·69	Methylic alcohol
Epicamphor	2·76	Methylic alcohol
αα-Dibromcamphor	3·13	Benzene
αα-Diiodocamphor	3·41	Benzene
Dihydrocarvone	3·30	None
Pulegone	2·76	None
1-Methyl-cyclohexan-3-one..	3·50	None
Nopinone	3·75	None
Pinonic acid	2·63	Methylic alcohol

The dispersion curves of such ketones for the most part cannot be expressed by the simple formula given by Drude—

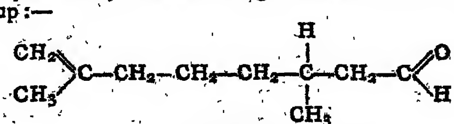
$$\alpha = \frac{k}{\lambda^2 - \lambda_0^2}.$$

Moreover, the rotations are influenced very largely by the nature of the solvent, just as is the case in substances showing anomalous rotatory dispersion.

On the other hand, it is well known that the ketones exhibit a general absorption band at about 3500 to 3800 A.U., whereas the saturated hydrocarbons and alcohols are practically diactinic for these radiations. We are therefore justified in concluding that the exaltation of the dispersion ratio $\frac{[\alpha]_F}{[\alpha]_C}$ in the ketones is intimately associated with the nature of the absorption spectra of these compounds.

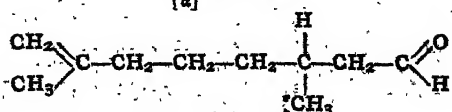
As a matter of fact, it was shown by Darmois ("Recherches sur la Polarisation Naturelle et la Polarisation Rotatoire Magnétique," Thèse, Paris, 1910) that camphor exhibits the typical form of anomalous dispersion in the neighbourhood of the ultra-violet absorption band.

Quite the same seems to be true in the case of *aldehydes*, which, like the ketones, show selective absorption in the ultra-violet, as was pointed out recently by Henry and others. Miss S. Matthiesen undertook at my suggestion the optical study of the following members of the citronellal group :—



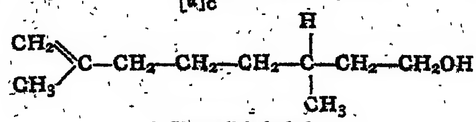
Citronellal.

$$\frac{[\alpha]_F}{[\alpha]} = 2·42.$$



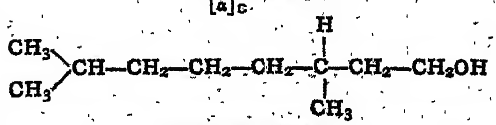
Dihydrocitronellal.

$$\frac{[\alpha]_F}{[\alpha]_C} = 2·40.$$



Citronellyl alcohol.

$$\frac{[\alpha]}{[\alpha]_C} = 2·04.$$



Dihydrocitronellyl alcohol.

$$\frac{[\alpha]_F}{[\alpha]_C} = 1·93.$$

It will be seen that the aldehydes examined possess almost as high a dispersion as many ketones, whereas the corresponding alcohols give quite normal dispersion ratios.

(To be continued).

CHEMICAL REACTIONS AT VERY LOW PRESSURES.*

I.—The Clean-up of Oxygen in a Tungsten Lamp.

By IRVING LANGMUIR.

About three years ago we had occasion to measure the amounts of gas given off by a tungsten wire when heated in a vacuum. We were surprised to find that amounts of gas as great as 1000 times the volume of the filament were apparently given off without any indication that the source of supply was nearing exhaustion. Careful investigation showed that the gas really came from the decomposition of the vapour of vaseline used on a stopcock, placed between the vacuum pump and the lamp containing the tungsten wire. The apparatus was therefore reconstructed, avoiding the use of stopcocks, but still the steady evolution of gas was observed when the filament was

* Paper read before the New York Section of the American Chemical Society. From the *Journal of the American Chemical Society*, xxxv. No. 2.

heated, although at a much smaller rate than previously. The source of this gas was found to be water-vapour given off by the glass of the bulb, which, coming into contact with the heated wire, produced hydrogen and oxidised the tungsten. The hydrogen was indicated by the McLeod gauge, whereas the water-vapour had not been. Further study showed that, to avoid such evolution of gases, the bulb must be heated to a temperature of at least 360° for an hour or more, after the lamp has been exhausted with a mercury pump. During this heating of the bulb, it is necessary to absorb the water-vapour with phosphorus pentoxide, or, much better, with liquid air. In order to be able to measure the quantities of gas accurately, we avoided the use of charcoal or any other porous material in connection with liquid air, but depended simply upon the low temperature to condense out water-vapour and carbon dioxide. For this purpose the tube connecting the lamp bulb with the rest of the apparatus was bent in the form of a U, which was kept immersed in liquid air during the whole of the experiment.

When these precautions were taken, it was found that relatively little gas was evolved when the filament was heated. The gas actually obtained from the filament was given off nearly instantaneously when the metal was heated for the first time to a temperature exceeding about 1500°. This gas usually amounts to from three to ten times the volume of the filament, and consists mostly of carbon monoxide. (All volumes of gas given in this paper are supposed to be measured at atmospheric pressure and at room temperature).

It may be of interest to give the results of the analysis of the gas given off from the bulb during the heating to 360°. Before heating the bulb, it was thoroughly dried out at room temperature over liquid air, and the gases obtained in this way were pumped out and rejected. Upon then heating the bulb to 360° for an hour, the gases given off were approximately as follows:—

300 cu. mm. water-vapour,
20 cu. mm. carbon dioxide,
4 cu. mm. nitrogen.

The bulb in this case was an ordinary 40 watt tungsten lamp bulb, made of lead glass. For a description of the method of analysis used, see *Journ. Am. Chem. Soc.* (1912, xxxiv., 1313).

In all of the work described in this paper, pressures were measured by a McLeod gauge, which was capable of measuring accurately to pressures as low as 0·01 micron of mercury (0·00001 mm. of mercury). From the known volume of the system and the pressure in it, we calculated the number of cm. of gas in the system, and the results in general are given in terms of quantity of gas rather than in pressures.

We have very carefully tested out the reliability of the McLeod gauge, and find that for all gases that are not condensed in a vacuum system at the temperature of −78° (solid carbon dioxide and acetone), the McLeod gauge gives extremely accurate results. But this gauge does not correctly indicate the pressure of such easily condensible gases as water-vapour, oil-vapour, or mercury-vapour, nor does it indicate correctly the pressure of any gas in the presence of even small amounts of water-vapour.

During some of the experiments on the evolution of gas from a tungsten wire, we noticed that if the filament was heated at a high temperature in gas which had previously been given off by the filament or obtained in any other way, the pressure would gradually decrease.

This clean-up of gas was known to exist in ordinary commercial tungsten lamps. There are several indications of this. In the first place, it was known that when a tungsten lamp is first lighted, after having been sealed off from the pump, there nearly always occurs a flash of blue glow in the lamp. This gradually becomes less intense, and finally, after flickering a few times, completely disappears. Other indications were obtained by attaching a adiometer to the lamp bulb. If, by swinging the lamp, the radiometer vanes were set in rotation, the time necessary for them to come to rest was at first only a few minutes. After the lamp had been burning several hours, the time necessary for the radiometer to stop increased to about an hour. Another and more accurate way of indicating this change in pressure is by means of quartz fibre, placed in the lamp bulb, close to the filaments, one end being attached to the glass close to the base of the lamp, and the other end swinging freely in the vacuum. In one typical experiment the pressure had been 0·018 micron, at the moment of sealing the lamp off from the pump. Upon shaking the lamp so that the fibre was set in vibration, and then placing the lamp in a quiet place, it was found that it took sixty-six minutes for the amplitude of the vibrations to become one-half the original amount. After this lamp had been running at 1 w.p.c. for about three hours, the time necessary for the amplitude to decrease 50 per cent had become 115 minutes. In other words, the amount of damping of the filament had decreased in the ratio of 1·75 : 1. This indicates that the pressure must have been at least as low as 0·010 micron, and presumably very much lower, because even in a perfect vacuum, the filament would probably not have vibrated much longer than 115 minutes to half amplitude.

Evidence of a clean-up of gas in presence of electric discharges is not uncommon. For example, it is well known that in the Moore tube, or in Geissler tubes in general, the vacuum steadily improves. The same observation has repeatedly been made in Röntgen ray tubes. It has been generally assumed that the gas in these cases is driven into the electrodes, or into the glass, or is absorbed by the metal which sputters from the cathode.

In order to gain a clear insight into the nature of the changes occurring in tungsten lamps during life, it was decided to investigate in some detail the causes of the clean-up in such lamps, and to study the behaviour of various gases in this regard.

Clean-up of Hydrogen.

When a tungsten filament is heated above 1300° K. in hydrogen, at low pressures, the hydrogen gradually disappears. (In this paper the letter K—Kelvin—will be used to denote absolute temperatures, in accordance with the recommendations of the Association International du Froid; see *Chem. Ztg.*, 1911, xxxv., 3). It has been shown in a previous paper (*Journ. Am. Chem. Soc.*, 1912, xxxiv., 1310) that this action is caused by the hydrogen becoming dissociated into atoms in contact with the filament, the atoms then being driven on to the bulb, and there held by adsorption, or some other cause. The hydrogen on the bulb is in a particularly active form, and is capable of reacting at room temperature with oxygen.

Since these experiments were made, further investigation of the clean-up of hydrogen has been carried on, and interesting results have been obtained. These, however, will be given in a subsequent paper.

Clean-up of Oxygen.

It is well known that metallic tungsten oxidises in the air at a red heat, and becomes covered with a layer of the yellow oxide, WO_3. At a white heat the oxide volatilises easily, forming a yellowish white smoke.

The first experiments with a heated tungsten filament in oxygen at a very low pressure showed that the oxygen disappeared fairly rapidly, without producing any darkening of the bulb. The rate of disappearance was proportional to the pressure of oxygen, but if the temperature of the filament was above 1500° K the rate did not seem to increase very rapidly with rising temperature. Also, when different lengths of filament were heated in the same bulb, the rate was found not to vary in proportion to the surface of the filament. Further investigation showed that the measured rate was to some extent limited by the rate of diffusion of the gas from the pump bulb and McLeod gauge over into the lamp bulb. At low pressures much

longer times are necessary for the equalisation of pressures than at ordinary pressures.

To avoid this resistance to the flow of the oxygen, several changes were made in the apparatus.

The apparatus used for the final experiment (Exp. 265) is diagrammatically represented in Fig. 1. The lamp bulb, B mas made large (1020 cc.), so as to have as large a proportion of the oxygen as possible in immediate contact with the filaments. Below the lamp is a tube, L, immersed in liquid air, which serves to exclude mercury vapour from the lamp. The lamp contained three sections of filaments

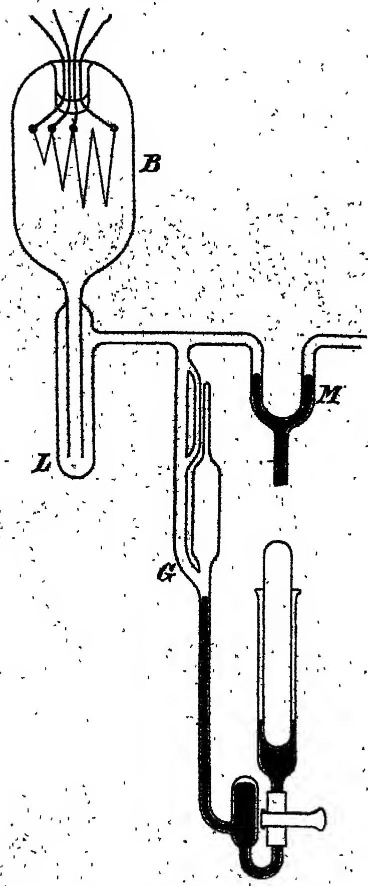


FIG. 1.

with four leading-in wires, so that any one of the sections could be heated to any desired temperature.

The diameter of the wire was 0·0394 mm. The lengths of the sections were :—

Section.	Length (cm.).	Area (sq. cm.).
a	5·4	0·067
b	14·6	0·181
c	47·0	0·583

The tubing between the bulb and the McLeod gauge G was made as short as possible, about 25 cm., and of large diameter (about 0·8 mm.) internal diameter, so that the resistance offered to the flow of gas would be as small as possible. For the same reason the volume of the McLeod gauge was made small (50 cc.). The apparatus was exhausted by a Töpler pump through the mercury seal M, through which also fresh supplies of oxygen were admitted.

After thoroughly exhausting the system (bulb heated one hour at 360°), and freeing from water-vapour and carbon dioxide, a definite amount of pure oxygen was admitted, and the seal M closed. After taking a reading of the gauge the current was suddenly turned on the filament, so as to heat it very rapidly to the desired temperature. Readings of the gauge were taken regularly every minute. With the longest section of filament, especially at the higher temperatures, the oxygen disappeared so rapidly that it was nearly gone in one minute. In these cases the current was turned off after a few seconds, and a reading of the gauge taken. The time intervals were measured by a stop-watch.

When the filament was heated to a temperature between 900° and 1200° K in oxygen, it immediately became coated with an oxide film which was at first straw-coloured, and gradually changed to dark blue and then to a dull brown. Simultaneously, the filament cooled off considerably, and ceased to be even red-hot, so that the current had to be increased considerably to maintain the original temperature. If the temperature was now raised to 1300°, bright spots appeared which gradually extended along the whole filament. When the filament had become uniform, it was found that the oxide film had entirely disappeared, and that a given current would heat the filament to the same temperature as originally.

The reason for the cooling of the filament is undoubtedly that the oxide is a better radiator of heat than the bright

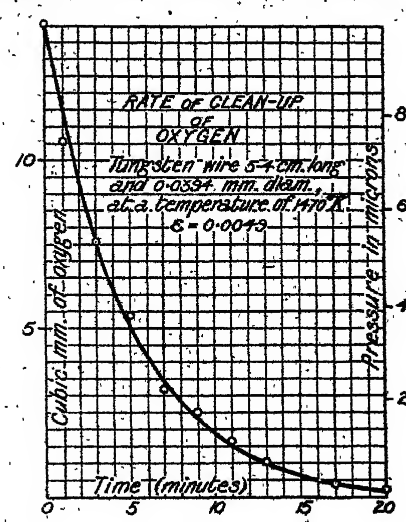


FIG. 2.

metal. The experiment indicates that the oxide volatilises in a vacuum at a temperature of about 1300°. The disappearance of the oxide is not due to dissociation of the oxide, for no evolution of gas occurs when the oxide film disappears.

At temperatures above 1250° the service of the filament always remains bright, even after long treatment in oxygen.

Fig. 2 gives a typical curve showing the way the pressure of oxygen decreases with the time. In this case section *a* of the filament was heated to 1470°. The ordinates represent the total amount (in cu. mm.) of oxygen gas remaining in the system (bulb, gauge, and tubing). The volume of the system being 1075 cc., 1 cu. mm. of gas corresponds to a pressure of 0·706 micron.

In practically every case the curves obtained were as smooth as this. Sometimes the gas would not completely disappear, but a slight residue, which proved to be nitrogen or carbon monoxide, would remain. In these cases this amount was subtracted from the other readings before

drawing further conclusions from the results. Before admitting fresh oxygen, these residues of foreign gases were always pumped out.

In some of the early experiments it had been found that the rate of clean-up of the oxygen was nearly independent of the temperature of the filament. One of the hypotheses that seemed to account for this was that the observed rate was simply the rate at which the oxygen came into contact with the filament.

It became of interest, therefore, to calculate from the kinetic theory at what rate a gas at low pressures would come in contact with a solid body.

Calculation of Greatest possible Rate of Clean-up.—Let us consider a square centimetre of a surface exposed to the pressure of a gas. According to the kinetic theory, the pressure is caused by the impact of the molecules. Let v be the average velocity with which the molecules strike the surface, and let m be the mass of the molecules which strike a square centimetre of surface per second. Now, according to the laws of mechanics, the force exerted by a series of collisions is equal to the momentum given up to the surface per unit time. Since the molecules leave with the same velocity with which they strike the surface, the momentum given up per second will be $m \times 2v$. This is equal to the pressure, whence—

$$m = p/2v \quad . \quad . \quad . \quad . \quad (1).$$

We can thus calculate the mass of gas which comes into contact with each sq. cm. of surface, if we know the pressure and the average velocity of the molecules.

According to the kinetic theory, the mean square velocity $\bar{v}^2$ of the molecules in a gas can be calculated from the equation—

$$p = \tfrac{1}{3} d\bar{v}^2 \quad . \quad . \quad . \quad . \quad (2),$$

where d = density of the gas.

The ordinary gas law $pv = RT$ can be written—

$$p = dRT/M \quad . \quad . \quad . \quad . \quad (3),$$

where M = molecular weight.

Combining this with Equation 2, we get—

$$\bar{v} = \sqrt{3RT/M} \quad . \quad . \quad . \quad . \quad (4).$$

If we assume that $\bar{v} = v$ then from (1) and (4) we may obtain the approximate formula—

$$m = \sqrt{M/RT} \cdot \frac{p}{\sqrt{3}} \quad . \quad . \quad . \quad . \quad (5).$$

Knudson (*Ann. Phys.*, 1908, xxviii., 999), by making use of Maxwell's distribution law, has avoided the above assumption, and has obtained equations which should be rigorously correct. Careful experimental investigations have proved the accuracy of the equation. From Knudson's formulæ, the following equation for the value of m is readily obtained,—

$$m = \sqrt{M/RT} \cdot p/\sqrt{2\pi} \quad . \quad . \quad . \quad . \quad (6),$$

which gives results 38 per cent larger than the previous formula.

To apply this formula to the case in hand, we place $R = 83.2 \times 10^6$ and for oxygen $M = 32$. For room temperature (25°) T is 298°, whence—

$$m = 14.3 \times 10^{-6} p.$$

Here p is to be expressed in dynes per sq. cm. If we express p in microns of mercury, we have—

$$m = 19.1 \times 10^{-6} p \text{ grms. per sec. per cm.}^2 \quad . \quad (7).$$

One cu. mm. of oxygen at room temperature and atmospheric pressure weighs 1.30×10^{-6} grms. Hence the rate at which oxygen, at a pressure of p microns, comes in contact with 1 sq. cm. of surface is $14.6 \times p$ cubic mm. per second per cm.^{2}

Now, in general, not all of the oxygen molecules which strike the filament will combine with it, but only a certain proportion will do so.

Let us represent by ε the ratio of the actual rate at which oxygen disappears to the rate which would prevail if the oxygen combined with the filament as fast as it comes into contact with it. Let q be the quantity of oxygen in the system at any time, t. Then we have—

$$dq/dt = \varepsilon \times 14.6\, pA \quad . \quad . \quad . \quad . \quad (8),$$

where q is expressed in cu. mm. at 298° K and atmospheric pressure.

p = pressure in microns of mercury.
A = area of filament in sq. cm.
t = time in seconds.
ε = fraction of molecules of oxygen which strike the filament that combine with it.

The quantity of gas q in the system can be readily calculated from the pressure and temperature of the gas and the volume of the system. In the present experiments the volumes of the different parts of the apparatus had been measured. If the lamp bulb is at room temperature we have—

$$q = pv/760,$$

where—

q = quantity of gas in the whole system in cubic mm. at 760 mm. pressure and 25°.
p = pressure in microns.
v = volume of system in cc.

When any part of the apparatus, for example, the lamp bulb, is heated above room temperature, then in calculating v we add the volumes of the various parts at room temperature and then add the product of the lamp volume by the square root of the ratio of the absolute room temperature to the bulb temperature. That is, if the bulb is at 300° (573° abs.), instead of taking its real volume, 1020 cc., we take $1020 \times \sqrt{298/573} = 734$ cc. Knudson explains fully the reason for multiplying by the square root of the temperature ratio (*Ann. Phys.*, 1910, xxxi., 205). We have thoroughly tested out this rule, and find that at pressures below about 10 microns it holds accurately. Let v_0 be the effective volume of the system, as calculated above, then we have—

$$q = pv_0/760 \quad . \quad . \quad . \quad . \quad (9).$$

By combining (8) and (9) we obtain—

$$dq/dt = 11{,}100\, \varepsilon\, q\, A/v_0,$$

whence—

$$\varepsilon = 207 \times 10^{-6} \frac{v_0}{At} \log \frac{q_0}{q} \quad . \quad . \quad . \quad (10).$$

Here q_0 is the amount of gas originally present and q is the amount after t seconds. v_0 and A are expressed in cm. units.

Results of Experiments.—Such a large number of experiments were made that it would be impracticable to give anything more than a summary of the results along with a few typical illustrations. A particular study was made of the effect of the following four factors on the rate of clean-up:—

1. Pressure.
2. Length of filament.
3. Temperature of filament.
4. Temperature of bulb.

Previous experiments with smaller bulbs had shown that the oxygen, even at the lowest pressures, combined with the filament to form WO_3. This was found by determining the loss in weight of a filament during treatment in oxygen and comparing this loss with the amount of oxygen which disappeared. An additional check was had by measuring the increase in the electrical resistance of the filament when cold, and also when heated. The specific resistance and the temperature coefficient of the resistance are not affected by heating in oxygen. From the changes in resistance the change in diameter could be calculated, and was found to agree well with that obtained by direct weighing after breaking open the lamp. In all the experiments the ratio of loss of weight to the weight of oxygen

cleaned up was very close to that calculated from the ratio W : 3O.

Only in rare instances was enough oxide deposited on the bulb to be visible; whereas, if the equivalent amount of tungsten had been on the bulb it would have been nearly black. This is an indication that the oxide must be of very light colour.

It is an interesting fact that when tungsten is heated to a very high temperature in nitrogen which contains traces of oxygen the blue oxide W_2O_5 is formed. In pure oxygen at high or low pressures this oxide never sems to be formed, except when the temperature is so low that the oxide remains on the filament instead of distilling off. This fact would indicate that the yellow trioxide is produced extremely rapidly directly on the filament, while the blue oxide is formed only by subsequent reduction of the trioxide.

All the experiments with oxygen gave results that were easily reproducible. The errors seemed to be only such as would occur from errors in the measurements of the temperature of the filament. In marked contrast with the experiments on the clean-up of hydrogen we never found any indications of fatigue in the clean-up of oxygen.

(To be continued).

THE SCIENTIFIC WEEK.

(From Our Own Paris Correspondent).

Sail Flying.

Dr. A. Magnan, Director of the Ecole des Hautes Etudes, has just presented to the Congress of the Sociétés Savantes a paper concerning a new apparatus invented by him with a view of enabling men to fly with sails, in the same way as flying birds, by utilising only the force of the wind, excluding all other propulsion whether m tive or muscular force. Flying with sails is a sort of continual swooping. The sailing bird does not appear to utilise any acquired speed. It does not appear to descend. Its wings are motionless in all directions. Sea birds especially employ this kind of flight to the almost entire exclusion of any other, but they can only do this with a good deal of wind, and it is when the wind is pretty strong that the most ideal sail-flying is to be observed. Many a time has man tried to imitate sailing birds. But, however, there is only one experimenter worthy of retaining our attention; it is Lilienthal. And in spite of thousands of experiments and trials he was only able, in employing ascending currents—that is to say, by flying against the wind—to cover very small distances. Dr. Magnan has tried fresh experiments of this kind. He has imagined an apparatus copying textually the sea-bird. He has succeeded in this very exactly, thanks to his preceding researches on the relation to the aeroplane with the dimensions that he had found in birds. He has already made some trials with a light apparatus carrying a mannequin, but he has come to the conclusion, like Lilienthal, that if it is important to imagine an ideal apparatus, it is also important to know how to manage it. One must learn how to drive such an apparatus as one learns how to ride a bicycle or to swim. This apparatus calculated for a given weight, including the pilot, has the following dimensions:—

	80 kilos.	90 kilos.	100 kilos.
Alary surface (M^2)	3·52	3·79	4·07
Weight of wings (kilos.)	15·560	17·500	19·450
Spread (metres)	6·02	6·27	6·49
Width of the wing to the middle (metres)	0·75	0·78	0·81
Length of tail (metre)	0·77	0·80	0·83
Weight of tail (kilos.)	3·680	4·140	4·600
Surface of tail (M^2)	0·42	0·46	0·49
Length of apparatus (metres) ..	2·49	2·59	2·69

M. Magnan has supplied this apparatus with a spread-tail so as to copy the example of certain birds who give to the tail and to the wings two contrary incidences, and thus remain motionless for hours together. Moreover, the wings of the apparatus, which are very pointed, have the exact form of the wings of sea-birds. They are also formed like gutters, one-third of the back of the wing being folded downwards at about 60°. M. Magnan, who is well aware of the difficulties that the pilot of such a monoplane must experience in order to realise the sail flying, makes his apparatus public, hoping that some audacious flyer would like himself to attempt to fly against the wind.

The Electrocution of Noxious Insects.

A new machine has just been invented by an engineer, M. Friggeri, for the destruction of insects. This electric machine has been tried at Palacios, in the province of Santa-Fé, in the Argentine Republic. The review the *Electricien* explains the machine imagined by M. Friggeri. It is a well-known fact that insects in general, and grasshoppers in particular, are good conductors of electricity. On a carriage that it is easy to transport, M. Friggeri places a spirit motor and a dynamo with an alternating current. At the back of the carriage a drum is placed, on which about 200 metres of insulated cable have been rolled. This cable carries the current to a metallic net or system fixed on to a little vehicle with two wheels, and which carries in its centre a transformer which is destined to raise the tension to 6000 volts and even more. The metallic circuit is disposed on the ground infested with the insects, then the circuit is established between a pole and the dynamo, formed by a stem of iron fixed into the ground and the net. After several trials, which have all been crowned with success, the experiments at Palacios were considered as decisive. Indeed, not only has it been possible to destroy the grasshoppers but also their eggs, which are to be found buried more than 9 centimetres deep in the ground. With the same apparatus provided with a metallic broom worked at the end of an insulatied handle, and which is joined to the positive pole of the transformer, it is also possible to completely clean the trees attacked by the *Diaspis pentagona* and other insects.

The Death of the Earth.

A mathematician, M. Veronnet, has just calculated that the living attire of the earth has only two million more years to live. The animals and plants will die. All life will cease progressively on the surface of our globe, and that will happen in less than twenty thousand centuries. And it is the cold that will bring about the death of our planet. This hypothesis has already been mentioned. But this is the first time that learned calculations have assigned such a short existence to terrestrial life. The deductions of M. Veronnet are, however, most rigorous. Two communications concerning them have been made to the Academy of Sciences, but have passed unperceived. M. Veronnet supposes, according to the theory of Helmholtz, that the sun contracts in cooling and constantly loses energy in the form of heat, in proportion to its surface and at the fourth power of its temperature. This is the law of Stefan. In speaking of the actual solar temperature, which is admitted to be of about 6200°, and in making certain hypotheses concerning the state of the condensation of the sun, M. Veronnet finds that the mean actual temperature of the earth must be of about 16° and 34° at the equator. These figures that result from calculations correspond pretty well to the reality. By looking backwards to the past, the learned mathematician perceives that two millions of years ago the sun must have had rays equal to one and a-half of its present rays. The quantity of heat that was dispersed on the earth was much greater than now. In the neighbourhood of the poles at a latitude of 80° the temperature of the surface of the earth must have been

about 90°. So, then, according to M. Veronnet, life could only have appeared from this period and starting from the poles. M. Veronnet has calculated also that in two millions of years the ray of the sun will be reduced by one-tenth. The earth will then be completely frozen, its average temperature being only at 0°. All life will then be impossible on the earth. Death will ensue, preceded probably by a return to a state of barbarity. The duration of life on the earth would thus be of about 4 millions of years, and we would then be actually at about the middle of the curve representing terrestrial life. As for the planet Mars, the same calculations indicate that it has long since been frozen, and that there is no more life on its surface. The speculations of M. Veronnet were the subject of a very interesting discussion at the last sitting of the Société Astronomique de France. M. Camille Flammarion accepts the hypothesis of M. Veronnet only with very great reserve. For him, geology takes the terrestrial life back more than twenty thousand centuries. Then, again, the planet Mars does not seem to him to be a frozen world. Another factor must also intervene in these calculations, according to M. Belot. This is the radio-active properties of bodies. The physicists have shown that the quantity of heat thrown off by radio-active bodies is so intense that the globe would be heated instead of being cooled if the terrestrial mantle contained, as far as a depth of 70 kilometres, the same proportion of radio-active elements as the rocks of the surface. But M. Pinsieux, Member of the Institute and Astronomer of the Paris Observatory, owns that physicists cannot know how radium acts at the formidable pressures that correspond to a depth of 70 kilometres. The *rôle* of radium in nature is not yet demon strated. Radiating matter has not yet intervened in laboratory experiments.

A New Method of Analysis.

A very ingenious method of analysis, enabling the estimation of substances susceptible of being precipitated in liquids, has just been imagined by M. Dienert, head of the water service of the City of Paris. He has combined the colorimetric process of Dubosq with the projection lantern. By looking in the half of the field of a telescope or lunette at a liquid containing matters in suspension, through a luminous cone, and in the other half of the field at a standard liquid, it is easy to see if the two liquids have the same coloration. By means of a colorimetric scale composed of standard liquids containing determined quantities of matters in suspension it is then very easy to compute, or at least to have a good idea of, the quantity of precipitate contained in a liquid. This same method can be utilised for determining the abundance of microbes in a vaccine or in any liquid, microbes being solids in suspension. M. Dienert applies this method to the estimation of matters contained in spring water, to the standardising of sulphuric acid, &c. The exactness obtained is as great as is the case with quantitative analyses. From 20 to 50 cc. of water are sufficient to make an analysis.

Phosphorescent Calcites.

M. Lacroix, Professor at the Paris Natural History Museum, has presented before the Academy a very interesting paper by M. Pisani, who has remarked that certain crystals of carbonate of lime can, under the influence of heat, acquire a remarkable phosphorescence which renders them luminous in the dark. Up till now it was thought that this phosphorescence was due to the presence of small traces of rare bodies. In the most part of calcites there are to be found, indeed, extremely small quantities of yttria; but M. Pisani has operated on absolutely pure crystals of carbonate of lime, and he has observed that when they are heated they become phos phorescent. This curious property of the crystals of carbonate of lime is, then, not due to the presence of rare elements.

PROCEEDINGS OF SOCIETIES.

ROYAL INSTITUTION.

Annual Meeting, May 1, 1914.

The Duke of Northumberland, K.G., President, in the Chair.

The Annual Report of the Committee of Visitors for the year 1913, testifying to the continued prosperity and efficient management of the Institution, was read and adopted. The Report of the Davy Faraday Research Laboratory Committee was read. Thirty three new Members were elected in 1913. Sixty-three Lectures and Nineteen Evening Discourses were delivered in 1913. The books and pamphlets presented amounted to about 289 volumes, making with 710 volumes (including periodicals bound) purchased by the Managers, a total of 999 volumes added to the Library in the year. Thanks were voted to the President, Treasurer, and Secretary, to the Committees of Managers and Visitors, and to the Professors, for their valuable services to the Institution during the past year. The following gentlemen were unanimously elected as Officers for the ensuing year:—

President—The Duke of Northumberland.

Treasurer—Sir James Crichton-Browne.

Secretary—Alexander Siemens.

Managers—The Right Hon. Lord Blyth, Dr. Horace T. Brown, J. H. Balfour Browne, Charles Hawksley, Major Edmund H. Hills, Dr. Donald William Charles Hood, Sir Edwin Ray Lankester, Sir Alexander Mackenzie, Robert Mond, the Right Hon. Lord Moulton, Edward Pollock, Sir James Reid, Bart., the Right Hon. the Marquis of Salisbury, Alan A. Campbell Swinton, and Harold Swithinbank.

Visitors—William R. Bousfield, Charles John P. Cave, Rev. Edward S. Dewick, Dr. William J. Gow, William A. T. Hallowes, John W. Jarvis, James Y. Johnson, H. R. Kempe, Dr. Adolph Liebmann, Carl E. Melchers, Dr. H. Forster Morley, Dr. F. W. Passmore, Charles E. S. Phillips, and Arthur J. Walter.

NOTICES OF BOOKS.

A Text-Book of Organic Chemistry. By A. F. Holleman, Ph.D., F.R.A.Amst. Edited by A. Jamieson Walker, Ph.D. (Heidelberg), B.A. and Owen E. Mott, Ph.D. (Heidelberg). Fourth English Edition.

A Laboratory Manual of Organic Chemistry for Beginners. By A. F. Holleman, Ph.D., F.R.A.Amst. Edited by A. Jamieson Walker, Ph.D. (Heidelberg), B.A. Second Edition.

New York: John Wiley and Sons, Inc. London: Chapman and Hall, Ltd. 1914.

When the first English edition of this work was issued ten years ago it was at once recognised by all who are interested in the teaching of organic chemistry to college students as a novel and valuable work, and it took a position in the front rank of text-books from which it has never been displaced. It is no exaggeration to say that its merits have been recognised all over the civilised world, for the original Dutch has been translated into seven languages, in many of which it has passed through several editions; thus there is clearly no need to enlarge upon its special features. In the latest edition much new matter has been added, and more attention has been paid to the application of physico-chemical methods in organic chemistry. The section on tautomerism has been re-written. The laboratory manual, which is issued in a separate volume, is an appendix to the text-book, and describes the experimental work which can suitably be performed either by students who are using the text-book

or as lecture table experiments. The order of the text-book is adhered to in it, and references are given to the paragraphs of the fourth edition.

Sugar Analysis By Ferdinand G. Wiechmann, Ph.D. Third Edition. New York: John Wiley and Sons, Inc. London: Chapman and Hall, Ltd. 1914.

In the third edition of this work the material has been cast into a new form, which the author hopes will render it most conveniently accessible in the several branches of the sugar industry. The first part deals with the analysis of sugar and of the materials used in its production, while in the latter part the analytical methods used in the control of cane and beet sugar manufacture and refining are treated in detail. Methods of calculating results are described fully with illustrative examples, in which, however, the author is not always careful to make it clear what units he is employing, as for example in the statement "Volume of metal = 5·0." The book contains a short résumé of the work of the International Commission for Uniform Methods of Sugar Analysis, down to the 7th Session held in New York in September, 1912.

Fuel. By J. S. S. Brame, F.C.S. London: Edward Arnold. 1914.

This book has been written chiefly for engineering students and engineers, and treats of fuel especially from the point of view of power production. Solid, liquid, and gaseous fuels are included, and a section is added on the analysis and calorimetry of fuels; in these chapters only the comparatively simple determinations usually required in commercial work are described. Of the solid fuels coal is naturally treated in the greatest detail, and all available data concerning the composition of the coals of the British Empire have been brought together. Among the liquid fuels a good deal of attention is paid to alcohol, the use of which will in all probability be greatly extended in the near future. The diagrams inserted to illustrate various processes are unusually clear, and the book is admirably adapted for the use of the technical man who needs a good general knowledge of the subject.

The Association of Teachers of Domestic Subjects. Annual Report, 1913.

This annual report for the year 1913 contains details of the conferences held by the various branches of the Association during the year and the reports of the committees. From a scientific point of view the chief interest of the report lies in the answers to various questions submitted by members. These questions relate to som- incompletely investigated or disputed practical problems in laundry work, cookery, &c., and an endeavour has been made to provide the correct scientific answers to them.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clviii., No. 11, March 16, 1914.

Syntheses by means of Sodamide. Preparation of Higher Homologues of Mono and Dimethyl Camphors and Corresponding Camphols.—A. Haller and Jean Louvrier.—By means of sodamide the monoalkyl and di-alkyl derivatives of camphor, both the symmetrical and asymmetrical compounds, and of camphol, can be prepared. The substituting power of the aliphatic radicles diminishes as one rises in the series. Only the mono-alkyl camphors give rise to oximes. The rotatory power of the monoalkyl derivatives increases with the molecular weight.

Direct Hydrogenation by Catalysis of Diaryl Acetones and Aryl Alcohols: Preparation of Polyaryl Hydrocarbons.—Paul Sabatier and M. Murat.—The diaryl acetones, benzophenone and its homologues, can be converted by direct hydrogenation over nickel into the corresponding diaryl hydrocarbons. Thus diphenylmethane is formed from benzophenone at about 300°. Similarly, the direct hydrogenation of aryl or polyaryl alcohols at 350° gives rise to the corresponding aryl or polyaryl hydrocarbons, according to the equation $RR'R''.COH+H_2=RR'R''.CH+H_2O$, where R is an aryl residue and R' and R'' are aryl or formic residues or hydrogen.

Ferrous and Chromous Metaphosphates.—A. Colani.—Ferrous metaphosphate can be prepared by acting on metaphosphoric acid with ferrous chloride or oxalate in a current of carbon dioxide. Ferrous phosphate, obtained by precipitating a ferrous salt with sodium phosphate, washing and drying in air, and then reducing with hydrogen, can be used as the ferrous salt. Ferrous metaphosphate, $Fe(PO_3)_2$, is a white powder very slightly greenish when in large quantities, insoluble in hydrochloric and nitric acids. Sulphurous acid attacks it very readily, sulphurous anhydride being liberated. All attempts to prepare chromous metaphosphate led to the formation of the chromic salt, $Cr(PO_3)_3$.

No. 12, March 23, 1914.

Syntheses by means of Sodamide. Preparation of Allyl Ketones derived from Alkyl Acetophenones and Pinacoline.—A. Haller and Ed. Bauer.—The authors described the preparation of allyl ketones, such as methyl ethyl allyl acetophenone, by preparing the sodium derivative of methyl ethyl acetophenone by means of sodamide, and then treating with allyl iodide. Allyl derivatives of benzylacetophenone can be prepared similarly, and pinacolin very readily gives allyl derivatives when its sodium derivative is treated with allyl iodide.

Use of Manganous Oxide for Catalysis of Acids. Preparation of Fatty and Aryl Acetones.—Paul Sabatier and A. Mailhe.—Manganese oxide, MnO, is an excellent catalyst for acids; it possesses the advantage of being cheap and it can be kept almost indefinitely. It can be used for the preparation of symmetrical or mixed acetones, and also to reduce the acids to give aldehydes. It is obtained by heating commercial precipitated manganous carbonate to 400° in methanol vapour in the catalysis tube, through which the vapours of the acid or mixtures of acids are led. The temperature is kept at 400° to 450°, and if the layer of oxide is 60 cm. long the acids are totally destroyed.

Potassium Tetroxide.—R. de Forcrand.—To prepare potassium tetroxide Vernon Harcourt's method was adopted. The metal is heated in a glass flask to 180° to 200° in a current of pure dry nitrogen, which is gradually replaced by air and then by oxygen. All traces of moisture must be avoided. A yellow deposit, K_2O_4, is thus obtained. The following values have been found when it is dissolved in very dilute sulphuric acid in a calorimeter:—K_2 sol. + O_4 gas = K_2O_4 sol. + 133·74 cal.; K_2O sol. + O_3 gas = K_2O_4 sol. + 46·94 cal. These numbers are both lower than those given by cæsium. As the atomic weight of the metal increases the heat of formation of the protoxide diminishes, but the heat of superoxidation (M_2O to M_2O_4) increases.

Density and Atomic Mass of Neon.—A. Leduc.—The author has found that the atomic mass of neon is exactly twenty times that of hydrogen, and hence = 20·15 for O = 16, and not 20·0 as stated by the International Commission. Aston (*Nature*, November 6, 1913) has stated that neon can be separated by diffusion into two gases, the densities of which correspond to the atomic

weights 19·9 and 22·1 respectively. The author suggests that the first gas is a mixture of neon and helium, and the second contains a large proportion of nitrogen.

Determination of Traces of Arsenic of the Order of a Thousandth of a Milligramme.—L. Moreau and E. Vinet.—The method depends upon the reaction $12AgNO_3 + 2AsH_3 + H_2O = 12HNO_3 + As_2O_3 + 12Ag$. The metal is deposited in the form of a ring. The apparatus consists of—(i.) a hydrogen generating flask; (ii.) a U-tube containing silver nitrate to wash the gas; (iii.) a U-tube containing the liquid to be investigated; (iv.) a small tube bent twice at right angles and containing an acetified solution of N/10 silver nitrate, at the bottom of which the ring is formed. The arsenic is determined by comparing the ring with that obtained with known quantities of arsenic in exactly the same experimental conditions.

Absorption of Carbon Dioxide from the Air by Chromium Hydrate.—Mil. Z. Iovitchitch.—Chemically pure chromium hydrate was exposed to the air for five or six days at 25° and the product was then analysed. It was found that its composition agreed with the formula $\begin{matrix} Cr_2(OH)_5 \\ Cr_2(OH)_5 \end{matrix} > CO_3 + 8H_2O$. This monocarbonate has a constant composition even at 100°. When dried to constant weight at this temperature it retains almost all its carbon dioxide.

Constitution of Potassium Carbonyl.—A. Joannis.—Potassium carbonyl deflagrates in presence of air or water, or when heated. The action of water upon it can, however, be studied by attacking it with water vapour at a tension of some millimetres, or by suspending it in liquid ammonia, and then adding water drop by drop, diluted with liquid ammonia. If the reaction is allowed to proceed slowly no explosions occur. A reddish yellow liquid is thus obtained, and from it glycollic acid can be separated. The reaction is $KCO.COK + 2H_2O = CH_2OH.COOK + KOH$.

Hydrates of Primary Amines.—Félix Bidet.—Normal amylamine, isoamylamine, and isobutylamine combine in the cold with the water vapour of the atmosphere, giving crystalline hydrates. In the case of isoamylamine the formula of the hydrate is $C_5H_{11}NH_2.2H_2O$. All the hydrates melt below 100°, and are remarkable for their high vapour tension, even below their melting-points.

Bulletin de la Société Chimique de France.
Vol. xv.-xvi., No. 5, 1914.

Rôle of Fluorine in the Animal Tissues.—Armand Gautier.—In the muscles, glands, nervous tissues, blood, and in the assimilating or nutritive secretions of the animal, fluorine is combined with phosphorus and the nitrogenous organic matter. One part of fluorine fixes 350 to 750 parts of phosphorus to the organic matter. In the bones, cartilage, tendons, elastic tissue fluorine is associated with 130 to 180 times its weight of phosphorus. Finally, in the nails, hair, feathers, epidermis, &c., the fluorine and phosphorus are present in the ratios in which they are found in minerals, especially in apatites.

No. 6, 1914.

Determination of the Constitution of Iodohydrines by the Action of Tertiary Amines.—MM. Tiffeneau and Fourneau.—When the two iodohydrines of phenyl glycol, $C_6H_5CHOHCH_2I$ and $C_6H_5CHICH_2OH$, are treated with tertiary amines two different reactions take place. In the one case, addition pure and simple occurs with formation for each iodohydrine of an iodohydrate of choline,—

$$\begin{array}{c} C_6H_5CHOHCH_2NRR'R'' \\ | \\ I \end{array} \quad \text{and} \quad \begin{array}{c} C_6H_5CHNRR'R''I \\ | \\ CH_2OH \end{array}$$

In the other case, elimination of HI takes place, but the hydrogen does not come from the hydroxyl group, and the result is a vinylic alcohol which isomerises to the corresponding aldehyde or ketone,—

$$C_6H_5CHOHCH_2I \rightarrow C_6H_5COHCH_2 \rightarrow C_6H_5COCH_3,$$
$$C_6H_5CHICH_2OH \rightarrow C_6H_5CH{=}CHOH \rightarrow C_6H_5CH_2CHO.$$

Thus the action of tertiary amines gives a double indication of the structure of iodohydrines; in the first place, aldehydes or ketones are formed in which the oxygen is present in the place occupied by it in the iodohydrine, and, secondly, a salt of choline is formed in which the nitrogen is situated in the place of the iodine. With the primary iodohydrine of styrolene the elimination of hydracid is the preponderating reaction, while with the secondary iodohydrine the addition reaction is the most important.

Transformation of Limonene into Carvomenthene and Menthane.—G. Vavon.—If limonene is shaken in an atmosphere of hydrogen in presence of platinum black the gas is rapidly absorbed, and all the limonene is transformed into menthane, $C_{10}H_{20}$. (The reaction takes place at the ordinary temperature and under atmospheric pressure). But without modifying the experimental conditions it is possible to hydrogenate the exterior double bond, and to prepare carvomenthene; it is only necessary to stop the reaction when 22·4 litres of hydrogen have been absorbed per molecule of limonene.

Action of Diazo Derivatives on Vegetable Oils.—P. Sisley and M. Frehse.—The salts of diazobenzene and of diazonaphthalene do not give colorations with vegetable oils, but the chloride of diazoparanitrobenzene gives very marked and stable colorations in many cases. If the reaction is negative (as with olive oil) the oil turns yellowish orange, owing to the formation of a little phenylnitrosamine and decomposition products of the diazoic salt. The colours obtained by different oils do not differ much in shade, being generally red or reddish brown, but since olive oil gives no reaction the purity of a specimen may be determined by means of the test.

MEETINGS FOR THE WEEK.

MONDAY, 11th.—Royal Society of Arts, 8. (Cantor Lecture). "Some Recent Developments in the Ceramic Industry," by W. Burton, M.A.
—— Royal Institution, 3. "The Last Chapter of Greek Philosophy—Plotinus as Philosopher, Religious Teacher, and Mystic," by The Very Rev. W. R. Inge, D.D.

TUESDAY, 12th.—Royal Institution, 3. "The Present State of Evolutionary Theory," by Prof. W. Bateson, F.R.S.
—— Royal Society of Arts, 4.30. (Cobb Lecture). "The Singing of Songs, Old and New," by H. Plunket Greene.

WEDNESDAY, 13th.—Royal Society of Arts, 8. "Glass Painting in Mediæval and Renaissance Times," by John A. Knowles.

THURSDAY, 14th.—Royal Institution, 3. "Identity of Laws, in General and Biological Chemistry," by Prof. Svante Arrhenius, D.Sc., &c.
—— Royal Society. "Various Inclinations of the Electrical Axis of the Human Heart—Part I.*a*, The Normal Heart, Effects of Respiration," by A. D. Waller. "Fossil Plants showing Structure from the Base of the Waverley Shale of Kentucky" by D. H. Scott and E. C. Jeffrey. "Controlling Influence of Carbon Dioxide in the Maturation, Dormancy, and Germination of Seeds," by F. Kidd. "Cultivation of Human Tumour Tissues *in vitro*." by D. and G J. Thomson. "Nutritive Conditions Determining the Growth of certain Freshwater and Soil Protista," by H. G. Thornton and G. Smith.
—— Society of Dyers and Colourists, 8. "Chemistry of Starch and its Transformations," by W. A. Davis. "Analysis of Malt Extracts," by W. P. Dreaper. "Temperature and Concentration as Affecting Hydration and Soda Absorption during the Process of Formation of Cellulose Monofils," by Clayton Beadle and H. P. Stevens.

FRIDAY, 15th.—Royal Institution, 9. "Plant Animals, a Study in Symbiosis," by Prof. F. Keeble, F.R.S.

SATURDAY, 16th.—Royal Institution, 3. "Bird Migration," by Prof. C. J. Patten, M.A.

THE CHEMICAL NEWS.

Vol. CIX, No. 2842.

CHABANEAU: AN EARLY WORKER ON PLATINUM.

By Prof. JAS. LEWIS HOWE.

Not long since M. Louis Quennessen of Paris (head of the old house of Des Moutis and Co., platinum refiners) directed my attention to an early worker on platinum, Pierre-François Chabaneau, whose name has so far escaped the historians of chemistry that I think it is not even mentioned in any English or German work, and has only appeared in the last edition of Moissan's "Traité de Chimie Minèrale." More recently, through the courtesy of M. Quennessen, I have received a copy of an all but unknown memoir, "Notice sur Chabaneau, Chimiste Périgourdin," par M. Jules Delanoue, printed at Périgueux in 1862, portions of which appear to be of sufficient interest to put on record. This biographical sketch was written in 1857, though not published till five years later, and has for its purpose "to call to the attention of our citizens the useful work, too little known, of a modest man, who unquestionably deserves the first place among the distinguished men whom Périgord has given to the world."

It may be noted that Périgueux is the capital of the old province of Périgord (now in part Dordogne) in south-west France, and has an interesting history going back to the time when it was the old Gallic town of Vesunna, the capital of the Petrocorii. Numerous remains of Vesunna are still in existence, especially baths, temples, an aqueduct, and fragments of the amphitheatre, mostly dating from its Roman occupation. The most notable building of Périgueux is the cathedral of St. Front, belonging to the Byzantine period, which bears quite a close resemblance to St. Mark's at Venice. The town has undergone many vicissitudes, having been taken by the barbarians in the fourth century, the Saracens in the eighth, the Normans in the ninth, the English in the fourteenth, and later restored to the French. It was a stronghold of the Calvinists in the Huguenot wars, and at this time was nearly laid in ruins. In the midst of an agricultural region, it is perhaps best known for its truffles and chestnut fed hogs, the latter being used in hunting for the former.

The early history of Chabaneau is a not unfamiliar one of precocity and hardship.

Pierre-François Chabaneau was born at Nontron (in north-western Dordogne) April 21, 1754. His family were respectable artisans, and he would undoubtedly have followed the obscure career of his parents had not his intelligence and pronounced love of study attracted the attention of his uncle, a monk of the order of St. Antony, at Aveyron (in south-central France, a hundred or so miles from Nontron). Young Chabaneau spent several years with this uncle, pursuing his studies along ecclesiastical lines, destined for the church. He was then sent to Paris for further theological study with the Oratorians, for his uncle was evidently by no means an ascetic. Here, for the sake of his kinsman, he entered upon his studies with great ardour and made such such rapid progress that he astonished his teachers; his theses were the admiration of all. Nevertheless, in spite of his brilliant successes, other influences were working on him, as is so often the case with such natures. He was not born for metaphysical studies; his inquiring disposition could not accommodate itself to the abstractions of scholastic philosophy. The unsupported scaffolding of theological hypotheses, the interminable verbiage, the halting arguments of the doctors, all failed to satisfy the spirit of the young Chabaneau and to accord with his ideas. He demanded mathematical arguments, the definiteness of figures, exact science, and not the science of paradoxes; his reason rebelled at the false ideas they sought to each him. In his dissertations he refuted his teachers by arguments which they could not controvert, and did it so thoroughly that the furious professors finally expelled their audacious scholar, as a punishment for his independence and for his success.

Behold now our young man in the streets of Paris, in the midst of the immense Babylon, without relatives, without friends, having neither experience of the world nor yet money! The six livres, which represented his whole fortune, had been expended in the purchase of a perruque, imperiously demanded by the customs of the times. He dared not return to his angry uncle, nor indeed had he the means for the journey. A kind Providence directed him to the abbé La Rose, to whom he related his story and revealed the extreme embarrassment in which he found himself. The worthy abbé was greatly interested and offered to place him as professor of mathematics in the Jesuit college at Passy (just out of Paris), of which he was the director. The young theologian, whose studies had been confined to Greek, Latin, and philosophy, was absolutely unacquainted even with arithmetic. He was greatly disappointed when he learned what his employment would be, but necessity compelled him to seize even this plank of safety; it was this or nothing. He unhesitatingly accepted the position, without venturing to acknowledge his complete ignorance of the subject he was to teach; he thought that perhaps by work and perseverance he might be able to fulfil his duties. He gave proof on this occasion of energy rare in one of his age, for he was only seventeen.

It is related of Jacques Amyot, the celebrated translator of Plutarch, that while he was a college servant he was possessed of such a desire for knowledge that he studied at night by the light of the fire. Young Chabaneau, whom chance and want compelled to teach others what he did not know himself, and who had great ambition to worthily carry out his task, passed the nights in preparation of the lessons for the following day. He hid his lamp, and then, when all the college world slept, lit it and worked till day. And so it was that, with indefatigable labour, aided by a powerful physical constitution, he made himself master of arithmetic, algebra, and geometry. Nor did he stop with these studies; the passion for knowledge dominated him. He studied experimental physics, natural history, and chemistry, that prodigious science which had just begun to give promise of the astounding wonders which have been realised in our day.

Just at this time was beginning the most active period in the work of Lavoisier, and it was the year before that he had presented to the Académie des Sciences his refutation of the supposed transformation of water into earth, in which the balance was used as an instrument of chemical research, and which soon led to the conception of the permanence of matter, and later to the overthrow of the phlogiston theory. This work of Lavoisier could not fail to make a great impression upon such a mind as that of Chabaneau.

His pupils made rapid progress; they wondered at the knowledge of the young professor, and the director, abbé La Rose, did not cease from expressing his satisfaction. . . .

Chabaneau was now about twenty years old, an age when is often born the love of independence. He knew that the knowledge which he now possessed would suffice to supply all his material needs. He therefore resigned from his position in the college of Passy, after having expressed his most sincere thanks to his benefactor, and, taking lodgings in the Rue des Mathurins, within the city, opened after the fashion of that day a course of public lectures, which met with great success.

Among the most assiduous of his auditors were the young sons of the Comte de Pena-Florida, whose fathe

had sent them to France to complete their education, and also to procure several professors for a great college for the nobility which he proposed founding at Bergara.

Bergara was a small city in the Basque province of Guipúzcoa in northern Spain, and near the Bay of Biscay. It afterwards came into some prominence as the place where the treaty was signed in 1839 between Spain and the Carlists of the Basque provinces. Of the subsequent history of the college I have been able to learn nothing.

The young nobles gained the affection of their professor and made him the most brilliant offers if he would accept the direction of the college founded by their father. For a long time Chabaneau resisted, but, finally yielding to the earnest solicitation of the young marquesses and other friends, he decided to exchange France for Spain. He immediately began the study of the Spanish language, and with such ardour that in a few months he felt that he had fully mastered it.

He remained three years at Bergara, devoted himself without relaxation to scientific study, and acquired such a reputation that the king, Charles III., wishing to locate him in Madrid, created for him a public Chair of Mineralogy, Physics, and Chemistry, lodged him in one of his palaces, and granted him an annual stipend of 2200 piastres (2400 dols.), a very considerable sum for that time.

The inauguration of his course took place in the presence of the king and all the court. This opening lecture had for its subject the utility and the future of science, and was so remarkable that a Spanish poet composed for the occasion an ode, dedicated to the learned professor. Impelled by the love of science, and wishing to justify the high favour in which he was held by the king, Chabaneau continued with great earnestness his scientific work. As he desired to enter into relations with all the learned men of Europe and to profit by their work, he recognised the necessity of studying English, Italian, German, &c. So energetic was he in his language study that at the age of twenty-five he was master of no less than eight languages, living or dead.

Charles III. provided Chabaneau with a valuable library and a laboratory, considered at that day "magnificent." All the spare moments remaining from his public instruction were devoted to the study of physics, and especially of chemistry. At this period Spanish America was sending to the mint at Madrid not only ingots of gold and silver, but also from time to time a mineral in the form of little white metallic grains, infusible and very heavy. The miners found it associated with gold and with diamonds (?) and called it *platina*, from its similarity to silver (*plata* in Spanish).

The government had no use for the platina, and, fearing it might be used to debase the coinage, ordered (ineffectually) that it should be buried when extracted from the ore. Meanwhile, in 1741, an Englishman named Wood gave the knowledge of platina to Europe; in 1750 Watson announced that it contained a metal hitherto unknown; in 1752 Sheffer, director of the Stockholm mint, and in 1754 Lewis, in London, dispelled all doubt regarding the fact that a new metal actually existed. Baron von Sickingen proposed a method for its extraction from the ore.

The new metal, platinum, thus obtained was in the form of a powder or sponge, which resisted fusion, even in the most powerful furnace, and was thus wholly useless in the arts. Chabaneau undertook the difficult task of obtaining platinum in metallic ingots, in spite of its infusibility. He recognised that this very infusibility would give great value to objects made of this new metal.

Several other chemists of the time had busied themselves with this same problem. The only hope of success appeared to be in alloying platinum with other metals, but this seemed to present insurmountable difficulties, owing in part to the impurity of the platinum ore, and also to the large amount of other metals necessary for its solution. It was early observed (von Sickingen says by Scheffer, who wrote in 1751) that a small amount of metallic arsenic caused platinum to fuse easily, but the ingot thus obtained was exceedingly brittle. Achard (1779) found that by heating this alloy for a long time at a high temperature the arsenic was gradually volatilised, leaving a mass of platinum in a malleable condition. While his communication to the Berlin Academy is entitled "Leichte Methode, Gefässe aus Platina zu bereiten," it was nearly ten years before practical application seems to have been made of the method, and though a letter appears in *Krells Annalen* in 1790 stating that platinum vessels can be bought cheaply of Jeanty in Paris, they were actually very rare and possibly never practically used until after the close of the century. Achard's method seems, however, to have been used industrially by Jeanty as late as 1820, though the method of Chabaneau, rediscovered by Knight and possibly independently by Cock also, came into general use in the first decade of the nineteenth century. The vessels made by Achard's method could never have been satisfactory, especially owing to the difficulty of completely removing the arsenic from the platinum.

Among the nobility who had interested themselves in the founding of the college at Bergara was the Marquess of Aranda. This man (minister of state and general, in 1787 ambassador to Paris) was distinguished among all the nobles for his devotion to science. He held Chabaneau in high esteem, and encouraged him strongly in his projected work upon platinum. He had the government turn over its whole supply of platinum ore to Chabaneau, and furnished him everything in his power for the laborious undertaking. Laborious, indeed, for even to day Dumas says "of all analyses, that of platinum ore is, without contradiction, the most difficult."

In spite of the regal luxury of his laboratory, Chabaneau found at that time in Madrid fewer resources than would to-day be offered by the most unpretentious laboratory in France. Chabaneau was obliged to prepare his own reagents and make his apparatus. Chemistry was still an empiric science, and Lavoisier had only just begun to bring order out of chaos. Further, at this time no one could have suspected that in addition to gold, mercury, lead, copper, iron, &c., the platinum ore contained five more metals, osmium, iridium, palladium, rhodium, and ruthenium, not discovered till 1803 and 1844. Chabaneau found himself contending with six metals where he supposed there was only one, platinum. Inevitable mistakes and innumerable disappointments naturally resulted. He had proved that platinum was malleable, yet occasionally he found it despairingly brittle (this was an alloy with iridium); he knew that it was infusible, incombustible, and unoxidisable, yet he was stupefied to see it at times burn and volatilise (this was the alloy with osmium).

The Marquess of Aranda, appreciating the great interest attaching to the industrial use of a metal of which Spain possessed all the mines, came often to Chabaneau's laboratory, and often found him discouraged and busying himself on other investigations. At such times Aranda, a most genial and lovable character, would console him, encourage him, and in the end bring him back to that which Aranda considered his great task, the investigation of "white gold," as it was then called. Chabaneau would take up with new zeal his tantalising work, and so passed days and nights, months, and years. At last he succeeded in surmounting all difficulties, his wearisome task was rewarded by the discovery of a process by which the metal could be purified. The effectiveness of the method was verified by several repetitions. The enchanted Marquess had him carry it out on a large scale, and came to the laboratory each day with increasing interest. Judge of his astonishment and horror when one day he found Chabaneau in a frenzy engaged in throwing out the door and windows his dishes, flasks, and ores, as well as all the solutions of platinum which he had prepared with so much trouble and difficulty.

The Castillian imperturbability of the Marquess only re-

doubled the French fury of the young chemist. "Away with it all. I'll smash the whole business," he cried in a mixture of French and the patois of Périgord. "You shall never again get me to touch the damned metal." And in fact he broke up all the apparatus of the laboratory.

Really this infantile fury was to some extent justifiable. No one knew then, and indeed few know now, that lime does not precipitate platinum in artificial light, but that in daylight the metal is completely precipitated by this re agent. Chabaneau, working with lime at night, had been enabled to precipitate all the other metals which were present in its solution, while his platinum was left unprecipitated and purified. Repeating the operation by day, platinum and all were thrown down, and he was completely at sea, without being able to suspect the reason.

Three months later, at the home of the Marquess of Aranda there appeared upon a table an ingot some 10 centimetres cube, with a beautiful metallic lustre; it was malleable platinum. The enthusiastic Marquess started to pick it up, but failed to move it. "You are joking," said he to Chabaneau, "you have fastened it down." "No, indeed," said the professor, and he raised the little ingot easily, though it weighed some 23 kilogrms. The Marquess had not thought that the light platinum sponge would thus appear as the heaviest of all (then known) metals.

Chabaneau's discovery consisted in compressing the platinum sponge while hot at the moment of its formation, and then hammering it several times while at a white heat. Since platinum is infusible at the highest temperature of a furnace, it is easily recognised how difficult it had been to convert the pulverulent metal into an ingot. This infusibility is, however, only relative, since Deville has since succeeded in fusing the metal with the oxygen-hydrogen blowpipe; but this property, added to a resistance to the action of acids equal to that of gold, evidently entitles platinum to rank with the precious (noble) metals.

It is to be noted that there were two necessary conditions for the preparation of malleable platinum, either of which was useless without the other. First, the metal must be obtained from the ore in a pure condition, for unless separated not only from the base metals, but also from the largest part of the other platinum metals, the sponge can not be welded into a malleable mass; second, while at a high temperature the sponge of pure platinum is easily compressed into a malleable ingot, at low temperatures it has no coherence. Virtually this process, generally attributed to Knight, was in use almost exclusively until the last third of the nineteenth century.

The king, who spent some of his leisure moments dabbling in science, often came to Chabaneau's laboratory and assisted in his experiments. He was very proud to have such a discovery made in his capital, and caused a commemorative medal to be struck in platinum. He also gave Chabaneau a life pension of 2800 piastres (3000 dols.), in addition to his annual stipend of 12,000 livres, but the pension was granted only on the express condition of residence in Spain, and was to be forfeited should Chabaneau leave the kingdom. The letters-patent bear the date of 1783, and thus establish the priority of Chabaneau's discovery officially and in an incontestable manner.

Chabaneau was for some time engaged in preparing large quantities of malleable platinum. Then his patron, Marquess d'Aranda, having been appointed ambassador to France (1787), he was prevailed on to accompany him to Paris, in order to convert under his auspices some of the new metal into ornaments for the crown. Jeanetty, goldsmith to the court of France, and a very able man, had been commissioned for this work, and he sought vainly to discover the process used by Chabaneau. He did, however, discover another method (alloying with arsenic), and employed it with such success that he founded in Paris a manufactory for platinum ware, which prospered down to 1820. At present the method of compression while hot, without alloying, is used, and that of Jeanetty has been abandoned.

It was only two years after this memoir was written that Deville and Debray perfected the method first proposed by Hare in 1838 of fusing platinum in the flame of the oxygen-hydrogen blowpipe. The memoir is somewhat misleading regarding the process of Jeanty (or Jeanetty), for while it is true that he did for many years manufacture platinum crucibles and other vessels by his method, it was early in the century entirely supplanted by the compression method, and it is doubtful if much practical application was ever made of it.

It is then to Chabaneau that belongs all the honour of having first discovered and employed on a large scale the only method which is in use to-day for preparing a metal so valuable for chemistry and the arts, and yet no contemporary writer has recorded the claim of our modest compatriot to the glory of this discovery. I apply to him the term modest, for in spite of all our entreaties he could never be persuaded to put forward his just claims. But to-day, as we have before our eyes the letters-patent of the Spanish government, bearing the date of 1783 and testifying to the discovery made by Chabaneau, we come to lay claim for him to the honour of incontestable priority, and to preserve his memory, ungratefully forgotten by his contemporaries.

About 1790 Chabaneau published a large work on the natural sciences in the Spanish language, which was to have been followed by several others, but which was complete as far as regards his speciality. This work, which demanded so much research, night work, and fatigue of every kind, gravely affected his health, and the court physicians prescribed a return to his native air and a period of complete repose. This rest and our climate affected him so favourably that in a few months his health was wholly regained, and he determined to renounce his pension of 15,000 francs in order to dwell in his fatherland, and to end in this quiet retreat, in the bosom of his family, a life, hitherto passed among strangers in the midst of the most assiduous labours.

Retiring to the country, near Nontron, he sought to live obscurely, but the jury of the central schools of France besought him to accept the chair of physics and experimental chemistry in the Ecole Centrale of Périgueux. The subjects were so seldom taught at this period that Chabaneau felt it the duty of a good citizen to accept the modest position. His course of lectures, which lasted two years, was printed at the expense of the administration, and published in year VII. by Canler at Périgueux.

On the suppression of the central schools he was offered a chair of chemistry at Paris, and his permission was sought to translate and publish his great work; but, well determined this time to live in his quiet retreat, he refused all these propositions, desiring only to live in solitude and to enjoy the repose so needed and so welcome after all his labours.

He died in January, 1842, at the age of 88, and left no descendant bearing his name. He lived tranquilly, isolated from the world, on his country place of Clara, near Nontron, dividing his time, like a sage of antiquity, between rural pursuits and philosophical study.

We knew him only in his declining years, but he was then a fine looking old man, with pleasing and regular features, bearing much resemblance to those of our good and lamented Béranger. His conversation was charming and always instructive. Friend and contemporary of Volney, of Cabanis, of Lavoisier, he was nourished upon their ideas and imbued with their spirit, and they were pleasingly reflected in his conversation.

Thus ends the story which has happily rescued us from oblivion the life and work of one of the gifted early workers in chemistry. That his name had been forgotten is doubtless chiefly due to his own modesty, but in part also to the fact that his labours were largely carried on in Spain, and his only important published work was in that language. Whatever may be the reason, the atmosphere of Spain has never been conducive to the development of science.—*Popular Science Monthly*, January, 1914.

A SIMPLE SUBSTITUTE FOR A LEAD CRUCIBLE OR CAPSULE.

By F. L. SHARP.

A PIECE of thin lead foil, such as is used for assay purposes, is carefully pressed into the interior of an ordinary porcelain crucible in such a manner that it adapts itself to the shape of the crucible. It is then suitable for testing for silicates. The substance, mixed with calcium fluoride, is put into the crucible, a little concentrated sulphuric acid added, and the whole carefully heated. The issuing vapours are allowed to impinge on a drop of water suspended in the loop of a platinum or lead wire. If a silicate be present a deposit of silica is at once seen in the drop of water. A thin strip of the lead foil may be rolled up and used as a substitute for the platinum or lead wire.

ANOMALOUS ROTATORY DISPERSION.*

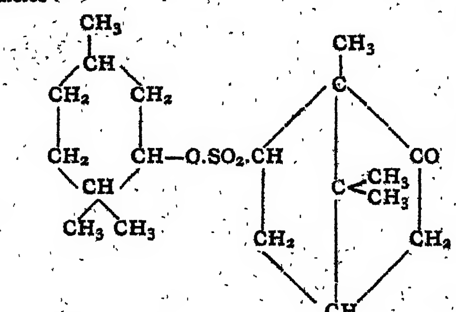
By Prof. LEO TSCHUGAEFF, Royal University, St. Petersburg.

(Concluded from p. 221).

3. We may now turn to the third and last type of anomalous rotatory dispersion.

It was recently shown by the author (L. Tschugaeff, *Berl. Ber.*, 1911, xliv., 2023; L. Tschugaeff and G. Glinin, *Berl. Ber.*, 1912, xlv., 2759) that anomalous dispersion may be produced by the *superposition of the partial rotations produced by two asymmetric complexes within the molecule of an active body*, the necessary condition being that these partial rotations should be of *opposite sign* and should possess *different dispersion ratios.*

As an example of bodies which belong to this type, menthyl β-camphorsulphonate may be cited, the two centres of activity being the menthyl and the camphor radicles :—



R. W. Wood ("Physical Optics," New York, 1911) has recently pointed out that there must exist a special case of anomalous dispersion which he denotes as "spurious," which is intimately related to the type just alluded to. Wood concluded from theoretical considerations that anomalous dispersion must ensue if we have two electrons in an active molecule, one in the infra-red and the other in the ultra-violet. If these electrons rotate in the same direction, the rotation may be expected to go through a zero value near the middle of the visible spectrum, whilst if they are of opposite sign, one being dextro-rotatory and the other lævo-rotatory, the rotation will have a minimum value. In Prof. Wood's opinion the case of tartaric acid is of this type.

It is well to bear in mind, also, that each anomalous dispersion curve must necessarily be influenced by the superposition of the consequent partial rotations if more than one asymmetric carbon atom (or generally more than one centre of activity) is present in the molecule of the active substance.

For this reason it is not surprising that there is no complete parallelism between the presence of an absorption band and the appearance of anomalous dispersion in the visible spectrum (L. Tschugaeff and O. Ogorodnikoff, *Zeit. Phys. Chem.*, 1913, lxxxv., 481).

Thus, menthyldixanthogenide,—

$$C_{10}H_{19}—OCS—S—S—CSO—C_{10}H_{19},$$

and bornyldixanthogenide,—

$$C_{10}H_{17}—OCS—S—S—CSO—C_{10}H_{17},$$

exhibit anomalous rotatory dispersion within the limits of the visible spectrum, whilst the fenchyldixanthogenide (isomeric with the bornyl derivative just mentioned and possessing a similar spectrum) does not possess this property.

In order to clear up the nature of the dispersion curves resulting from optical superposition it is necessary to examine, first, if the superposition rule is generally valid, and, secondly, in what degree these partial rotations themselves are influenced by mere constitutional factors.

The principle of optical superposition, first suggested by van 't Hoff ("Lagerung der Atome in Raume," 1908, III. Auff., Braunschweig), was subsequently subjected to an experimental test by Guye and Gautier, and by Walden, and recognised as valid (*cf.* van 't Hoff, "Lagerung der Atome in Raume," 1908, III. Auff., Braunschweig). Recently, however, Rosanoff (*Zeit. Phys. Chem.*, 1906, lvi., 565) and Patterson and his pupils (*Journ. Chem. Soc.*, 1906, lxxxix., 1039; 1907, xci., 705) put forward theoretical objections and experimental evidence against the validity of this principle, their arguments being based on a comparison of the optical rotation produced by the methyl esters of the isomeric diacetyltartaric acids.

According to the theory of optical superposition the rotation of the ester corresponding with mesotartaric acid should be equal to half of the sum of the rotations produced by the ester of *d* and *l* tartaric acids. The maximum departure from the theoretical value in the experiments of Patterson amounted to 18 per cent. But the rotation values of these esters are largely influenced by the nature of the solvent used, and van 't Hoff suggested therefore that analogous experiments should be made in more comparable conditions.

As a matter of fact, experiments performed by Mr. Glebko (*Berl. Ber.*, 1913, xlvi., 2752) at my suggestion with *l*-menthyl and fenchyl urethanes of the isomeric diethyltartrates gave much better agreement with theoretical values, the difference varying from 1 to 5 per cent. Consequently, the superposition rule seems to be valid at least to a first approximation.

Experiments quite recently performed in my laboratory have shown that the dispersion curve of an active substance is influenced not only by the absorption bands, but by the distance of the centres of activity from the chromophores of the active molecule. Thus, a chromophore group situated in the neighbourhood of a centre of activity may produce anomalous dispersion within the limits of the visible spectrum, whilst if sufficiently remote from such a centre its influence on the shape of the dispersion curve may be small or negligible.

To take an instance, of the two metameric esters corresponding to *l* menthol—

$$C_{10}H_{19}—OCS—S—CH_2—COO—CH_2\ C_6H_5 \quad . \quad I.$$
$$C_6H_5—CH_2—OCS—S—CH_2—COOC_{10}H_{19} \quad . \quad . \quad II.$$

it is only the first (I.) which shows anomalous dispersion in the visible region, the dispersion of the ester II. being quite normal. (This work—not yet published—was performed at my suggestion by Mr. W. Lebedinski).

Now, in the ester I. the chromophorous group CS—S is separated from the active radicle, $C_{10}H_{19}$, only by a single oxygen atom, whilst in the second ester these two radicles are separated by a chain of three atoms,—

$$—C—C—O—.$$

* A Contribution to a General Discussion on "Optical Rotatory Power," held before the Faraday Society, March 27, 1914.

The above conclusion is quite analogous with a rule put forward by the author some sixteen years ago (*Berl. Ber.*, 1898, xxxi., 360, 1775, 2451; *Journ. Russ. Phys. Chem. Soc.*, 1897, [II.], xxix., 122, 227; 1898, xxx., 18, 51, 188, 217; 1902, [I.], xxxiv., 606) for optical rotations corresponding with one definite ray of the spectrum, namely, the D line of sodium. According to this rule the influence of an inactive substituent introduced into an active molecule at a point sufficiently remote from the centre of activity is very small, but its influence attains its highest value if the place occupied by the substituent is in the neighbourhood of the inactive complex.

NOTE.—These conclusions are by no means altered by the results of the very beautiful work of Messrs. Pickard and Kenyon, which show secondary irregularities in the rotation curves in homologous series at points at which the carbon chain can return upon itself (R. H. Pickard and J. Kenyon, *Journ. Chem. Soc.*, xcix., 45; ci., 620, 1427; ciii., 1923. See also the very remarkable Presidential Address by P. F. Frankland, (*Journ. Chem. Soc.*, ci., 656).

It is particularly noteworthy that the radicles, the introduction of which into the molecule of an active substance causes the rotation values for the most part to be raised (*e.g.*, the radicles with a double linkage, the aromatic groups, &c.), and the chromophores which are responsible for anomalous dispersion possess the same chief feature, for they are both *unsaturated* groups.

In the author's opinion the modern electronic theory of rotatory polarisation and dispersion created by Drude ("Optik," 1906), is capable of throwing some light on this question, and of giving a rough idea of the influence which the constitutional factors just considered may exert on the sweep of the dispersion curve.

Drude has put forward the idea that optical rotation is due to a peculiar form of electronic motion. He assumes that the dispersion electrons which are capable of being set in vibration by the impacts of the light waves are forced in active bodies to move to and fro in a spiral path instead of along straight lines, the direction of the motion corresponding with the sign of the rotation. This motion is obviously due to the asymmetric distribution of matter within the molecules of the active compounds.

Drude makes no special hypothesis as to the position occupied by the active electrons, but it seems reasonable to suppose that the most active of them are attached to the asymmetric carbon atom itself, or are situated in the immediate neighbourhood of the centre of activity. As regards the other electrons which come into play in rotatory dispersion, we can assume that their activity is diminished with increasing distance from the asymmetric complex.

In the spectrum of colourless saturated organic compounds there seems to exist a very deep band (or several bands) in the inaccessible ultra-violet, and it is very probable that to this band is due the general shape of the "normal" dispersion curve, its "anomalous" portion being restricted to the neighbourhood of the band.

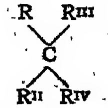
This view is in accordance with the results recently obtained by T. M. Lowry in his very remarkable investigations on both magnetic and optical rotatory dispersion (*Phil. Trans.*, 1912, ccxii., 261; *Journ. Chem. Soc.*, 1913, ciii., 1062; T. M. Lowry and T. W. Dickson, *Journ. Chem. Soc.*, 1913, ciii., 1067; *Proc. Chem. Soc.*, 1913, xxix.). Lowry pointed out that the dispersion of many colourless active compounds in the visible spectrum may be represented by means of an equation given by Drude with but two constants,—

$$a = \frac{k}{\lambda^2 - \lambda_0^2}$$

λ_0 being the wave-length of the remote ultra-violet band.

If, however, the substance in question possesses another absorption band within the limits of the visible spectrum, the dispersion curve becomes anomalous in the accessible spectral region, and even if the selective absorption occurs in the near ultra-violet, as in the case of the ketones above mentioned, the shape of the curve corresponding to the visible part betrays the neighbourhood of an absorption band, the dispersion ratios assuming abnormally high values.

Let us first turn our attention to colourless compounds, and consider in what manner the different inactive radicles of an asymmetric molecule—



containing but one asymmetric carbon atom, can influence the rotation value and the shape of the dispersion curve.

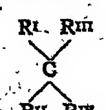
As we have seen, the chief part of the optical rotation will be produced by the electron (or electrons) attached to the asymmetric carbon atom itself, and will remain in direct relation to the deviation of the spiral path along which the electron moves from a straight line. Now, it may be admitted that this deviation should be proportional to the degree of asymmetry of the molecule as measured by the product of the differences of four constants, K_1, K_2, K_3, and K_4, corresponding with the four groups R^{I}, R^{II}, R^{III}, and R^{IV} of the molecule $CR^{I}R^{II}R^{III}R^{IV}$, as was originally suggested by Ph. A. Guye ("Etude sur la Dissymétrie Moléculaire," Geneva, 1891) and by Crum Brown (*Proc. Roy. Soc. of Edinburgh*, 1890, p. 181).

$$P = (K_1 \quad K_2)(K_1 - K_3)(K_1 - K_4)(K_2 - K_3)(K_2 - K_4)(K_3 - K_4).$$

Perhaps we should not be far from the truth if we assume further with Guye that the variables $K_1 \ldots K_4$ are functions of the masses of the radicles attached to the asymmetric atom, although we do not know the exact nature of this function; but in any case, if these four groups differ materially in their degree of saturation, we shall still have to consider the influence of another constitutional factor on rotation; thus, it would be expected that strongly unsaturated radicles containing free-movable electrons would exert a considerable influence on the electric field produced by the molecule, the differences $K_1 - K_2 \ldots$ being much larger if K_2 corresponds with a saturated group and K_1 to an unsaturated one than if both the groups are nearly equally saturated.

From this point of view it may easily be understood why the influence of unsaturated groups on the rotation values is considerable only when in immediate proximity to the asymmetric carbon atom. (It seems to be permissible in this case, at least to a first approximation, to compare the effects produced on the rotation by different substituents entering into the molecule for one determined wave-length, *e.g.*, for the D sodium line, as has so often been done).

On the other hand, the rotation and dispersion produced by an active molecule—



may be influenced by the vibration of the electrons attached to the radicles, R^{I}, R^{II}, R^{III}, R^{IV}, as well as to the asymmetric carbon atom itself, for the asymmetry of the field within the molecule must cause all these electrons to move along spiral paths. Consequently, each radicle must contribute by means of its electrons to the value of the optical rotation produced by the molecule as a whole, and (the free periods of these electrons being, in general, different) also to the resulting dispersion. It may be noted also that it is by no means necessary that the electrons in the four radicles and in the central atom should rotate in the same direction. Consequnely, it seems to be possible that certain bodies containing but one asymmetric carbon atom can exhibit anomalous rotatory dispersion. The anomaly will be due, in this case, to the superposition of the effect produced by the electrons

attached to the different radicles of the same molecule. The question as to whether such cases can be realised in practice can be settled only by experiment, but it is possible that some cases of anomalous rotatory dispersion quite recently notice by R. H. Pickard and J. Kenyon should be classed in this category (*Proc. Chem. Soc.*, 1913, xxix., 296).

Time will not permit of further discussion of the influence of chemical constitution on the rotatory dispersion in active compounds, but I should like before concluding to touch briefly upon an allied question which claims a very considerable interest.

It was pointed out by Chr. Winther (*Zeit. Phys. Chem.*, 1902, xli., 161; 1903, xlv., 331), and by P. Walden (*Berl. Ber.*, 1905, xxxviii., 345; *Zeit. Phys. Chem.*, 1906, lv., 1), that the dispersion curves of several anomalously dispersing bodies are largely influenced by the temperature at which their rotations are taken and by the nature of the solvent used.

It seems to be the current opinion that this particular behaviour is due to a displacement of equilibrium between the two (or more) different kinds of molecules which are assumed to constitute the active substance.

A quite different hypothesis, however, was put forth recently by R. W. Wood, the distinguished American physicist. He assumes, as previously mentioned, that the anomalous dispersion of tartaric acid may be due to the existence of two active electrons in its molecule.

This hypothesis is in complete accord with the view just put forward, that several electrons may be active in a molecule containing but one asymmetric carbon atom; in which case the rotatory power as well as the dispersion of the substance in question will be equal to the sum of the effects produced by several active electrons.

On the other hand, it is very probable (1) that the configuration of the molecule, and consequently the degree of asymmetry of the corresponding asymmetric field, is a function of the temperature, and (2) that the intensity of this field is not equally influenced in its different parts by the same rise of temperature.

It seems to be quite possible therefore that the influence off different active electrons may become dominant at different temperatures, and that a substance which possesses normal rotatory dispersion at a certain temperature t_1 may become anomalous at another temperature t_2. It is, however, very d fficult in the present state of our knowledge to distinguish between such a case and the case of a mixture of two active bodies which present anomalous dispersion at certain temperatures only.

Similar considerations may apply in relation to the influence of solvents on anomalous rotatory dispersion. It is therefore easy to understand that, from the above point of view, active bodies which are especially sensitive to the influence of the temperature and of the solvents must have a marked tendency to present the phenomenon of anomalous rotatory dispersion.

NOTE.—Quite recently R. H. Pickard and J. Kenyon stated that certain esters containing but one asymmetric carbon atom exhibit anomalous rotatory dispersion at high temperatures as well as in several solvents (*Proc. Chem. Soc.*, 1913, xxix., 296). In the author's opinion this effect may be due to the intramolecular superposition of the effects produced by several active electrons.

Since nearly the whole of the experimental data concerning the influence of temperature and of the solvent on anomalous rotatory dispersion have been derived from derivatives of tartaric and malic acid (*Zeit. Phys. Chem.*, 1913, lxxxv., 481, 553), it seemed advisable to undertake analogous experiments with active bodies representing the different types of anomalous dispersion above mentioned. This work has been carrred out in my laboratory in conjunction with Messrs. Piqoulewsky, Pastanogoff, and Ogorodnikoff. (The details of the experiments of R. H. Pickard and T. Kenyon above mentioned are not yet available).

The results obtained have two important bearings:—Firstly, they show that sensibility to the influence of temperature and to the nature of the solvent is not confined to colourless bodies exhibiting anomalous dispersion of the type of tartaric acid, but occurs also in substances exhibiting Cotton's phenomenon and in those which possess anomalous dispersion due to intramolecular optical superposition.

It may be noted also that this sensibility can be very different in closely related substances. To take an instance, the dispersion of the thioanhydride of the menthylxanthogenic acid, $C_{10}H_{19}O—CS—S—CS—O—C_{10}H_{19}$ is very considerably influenced by temperstüre, while the sensibility of the corresponding fenchyl derivative is quite insignificant, in spite of the fact that both dispersion curves are nearly identical in shape.

Secondly, it follows from our experiments that in many cases the anomalous dispersion curves are shifted by the influence of temperature or by the nature of the solvent in the same direction as in the case of tartaric acid and its esters. For instance, the behaviour of the thioanhydride of menthylxanthogenic acid, $C_{10}H_{19}—OCS—S—CSO—C_{10}H_{19}$ towards temperature and the influence of different solvents on the dispersion of menthyldixanthogenide, $C_{10}H_{19}OCS—S—S—CSO—C_{10}H_{19}$, may be cited. In both cases the curves are at the same time raised and shifted to the violet end of the spectrum, precisely as Winther and others have observed is the case in the tartaric series. This analogy is a very remarkable one, and whatever its final interpretation may be, there is no doubt that there must exist some intimate relation as to the origin of the anomaly in both cases.

CHEMICAL REACTIONS AT VERY LOW PRESSURES.*

I.—THE CLEAN-UP OF OXYGEN IN A TUNGSTEN LAMP.

By IRVING LANGMUIR.

Continued from p. 225.

1. *Effect of Pressure.*—In every case the value of ϵ was found to be practically independent of the pressure. For example, in the experiment from which the curve in Fig. 2 was obtained, the following values of ϵ were obtained:—

Time, t.	Quantity of O_2, q.	ϵ.
0	14·09	
1	10·58	
3	7·59	0·0051
5	5·42	
7	3·20	
9	2·50	0·0045
11	1·66	
13	1·05	
17	0·40	0·0049
20	0·25	
23	0·18	

The curve given in Fig. 2 was calculated from Equation 10 by taking $\epsilon = 0·0049$, $A = 0·067$, $v_0 = 1075$. The equation thus becomes:—

$$\epsilon = \frac{0·0554}{t} \log \frac{q_0}{q},$$

where t is the time in minutes. It was from this equation also that the values of ϵ in the above table were calculated. It is seen from Fig. 2 that the calculated curve agrees well with the points determined by experiment.

This independence of ϵ from the pressure has been tested and found to hold for pressures as high as 50 and as low as 0·2 micron.

* Paper read before the New York Section of the American Chemical Society. From the *Journal of the American Chemical Society*, xxxv., No. 2.

The fact that ϵ is independent of the pressure means simply that the rate of clean-up is strictly proportional to the pressure; in other words, the reaction acts like a monomolecular reaction.

2. *Effect of Length of Filament.*—Sections A, B, and C were respectively 5, 15, and 47 cm. long, yet as is shown clearly in Tables I., II., and III., the values of ϵ obtained were practically the same from each. This simply means that the rate of clean-up is strictly proportional to the surface of the filament.

TABLE I.—*Values of ϵ from Exp.* 265.

Temp. of filament.	Section A.	Section B	Section C.
1270° K	0·0010	0·0011	0·0014
1470	0·0049	0·0049	0·0055
1470	—	—	0·0059
1570	0·0092	0·0091	0·0099
1770	0·021	0·024	0·027
1770	0·025	0·027	0·027
1770	0·026	0·024	—
1770	0·028	—	—

TABLE II.—*Effect of Heating Bulb. Values of ϵ from Exp.* 265.

Temp. of filament.	Section B. Temperature of bulb.		Section C. Temperature of bulb.	
	23°.	300°.	23°.	300°.
1270° K	0·0011	0·0012	0·0014	0·0013
1470	0·0049	0·0042	0·0057	0·0053
1570	0·0091	0·0078	—	—
1770	0·0250	0·0183	—	—

TABLE III.—*Values of ϵ from Exp.* 265.

Temp. of filament.	Section A.	Section B.	Section C.
900—1070° K	0·00036	0·00035	0·00033
1270	—	0·0016	0·0015
1770	0·022	0·026	0·023
2020	0·043	0·049	0·046
2290	0·095	0·068	0·080
2340	—	—	0·084
2520	0·122	0·075	0·090
2770	0·15	0·095	0·115

3. *Effect of Temperature of Filament.*—In Tables, I., II., and III. are given the values of ϵ from Exp. 265, in which the apparatus was arranged as indicated in Fig. 1. The separate runs were made in about the order given in the table. The temperatures were obtained from photometer measurements on a lamp made from another piece of the same wire. From the candle power per sq. cm. of surface the temperature was obtained, and from this a curve giving the relation between current and temperature was plotted by use of a formula previously given (*Trans. Am. Electrochem. Soc.*, 1911, xx., 233). After the lamp in Exp. 265 had been exhausted and the filaments aged by heating one-half hour at a very high temperature, the relation between voltage and current, and hence temperature, was obtained. From these data a curve was plotted giving $V\sqrt{A}$ for each of the filaments as a function of the temperature. (Here V = volts; A = ampères). This function remains constant even when the diameter of the filament changes between wide limits, and it was by its use that the temperature measurements were made after the filament had been attacked, to any serious extent, by the oxygen. Towards the end of the experiment the resistances (at 25°) of the three sections of the filament had increased up to the following percentages of the original resistance:—

Section A increased to 142 per cent.
Section B increased to 191 per cent.
Section C increased to 121 per cent.

The areas A were therefore reduced as follows:—

Sec. A reduced to 84 per cent of original surface.
Sec. B reduced to 72 per cent of original surface.
Sec. C reduced to 90 per cent of original surface.

In Table III. corrections were made in ϵ to correspond to these changes in surface. The filaments were reduced very uniformly in diameter, as was apparent from the uniform intensity of the light emitted from them.

The irregularities in the values of ϵ at higher temperatures and in the latter runs are probably due to errors in temperature measurements and to the difficulties in measuring the extremely high rates of clean-up which occurred at the highest temperatures.

TABLE IV.—*Rate of Clean-up of Oxygen at Various Temperatures.*

Temp. K.	ϵ observed.	ϵ cal. by (12).	ϵ cal. by (26).
1070° K	0·00033	0·00016	0·000171
1270	0·0011	0·00123	0·00124
1470	0·0053	0·00525	0·00528
1570	0·0094	0·0095	0·00953
1770	0·0255	0·0256	0·0256
2020	0·049	0·066	0·0664
2290	0·095	0·148	0·150
2520	0·12	0·26	0·264
2770	0·15	0·42	0·426
3000	—	0·60	0·64
3500	—	1·16	1·28

At 2770° K the rate of clean-up was so rapid with Section C that the quantity of oxygen decreased from 14·90 cu. mm. to 2·64 cu. mm. in three seconds. With Section A, at the same temperature, the gas changed from 7·55 to 2·88 cu. mm. in twelve seconds.

The second column of Table IV. gives the most probable values of ϵ taken from Tables I., II., and III. The data for temperatures from 1220 to 1770 are obtained by taking the means of the values in Table I., these being considered the most reliable, as the filaments had not been altered much by oxidation during these runs. For temperatures above 1770 the highest of the values in Table III. were chosen, for the possible errors would seem to make the observed values too low.

The rate of increase of ϵ with the temperature agreed well with Arrhenius's formula—

$$d \ln \epsilon / dT = A/T^2 \quad . \quad . \quad . \quad . \quad (11).$$

The following equation, obtained from the above by integration and choice of suitable constants, was found to be in excellent agreement with the experimental results obtained between 1220 and 1770°,—

$$\log \epsilon = 1·76 - 5940/T \quad . \quad . \quad . \quad . \quad (12).$$

The values of ϵ calculated for various temperatures from this equation are given in the third column of Table IV. The deviation of the observed from the calculated results at high temperatures is to be expected, as the above equation leads at 3500° to values of ϵ above unity, and this we know, from the kinetic theory, must be impossible.

(To be continued).

THE SCIENTIFIC WEEK.

(From Our Own Paris Correspondent).

THE RUST OF CEREALS.

Prof. Gaston Bonnier has presented two papers before the Academy of Sciences on the question of the propagation of the rust of corn by the germs of the fungus mixed with the grain of the cereals. The first of these papers is by M. Eriksonn, Professor at the University of Stockholm; the second is by M. Beauveric, of the University of Nancy. M. Eriksonn is a partisan of the propagation of the rust by the grain itself containing kinds of cysts of rust. For M. Beauveric, who maintains, on the contrary, that the disease could be propagated by the germs to be found on the surface of the seeds, the question is not solved. It is easy to understand that these researches are of the highest importance for agriculture. But whether it be in one way

or the other that the disease is propagated, it is now an acquired fact that the passage of the fungus of rust of corn by the "epine vinette" or barberry thorn is not indispensable to the propagation of the disease from one year to another.

CULTURES OF ASPERGILLUS NIGER.

Prof. Gabriel Bertrand has examined the influence of solutions of salts of silver on the culture of the black mildew or smut of *Aspergillus niger*. This influence is pernicious as far as the dose of one-tenth of a milligrm. per litre. Below that, although the experiments have been continued to an extraordinary weak dilution of a molecule-grm. of argentic salts in 10 milliards of trillions of litres, it is impossible to detect the least acceleration of growth, contrary to what might have been expected according to the theory of toxic excitement, which is thus contradicted.

CAST IRON AND STEEL IN FRANCE.

A very interesting statistic on the production of cast iron and steel by French metallurgy in the year 1913 has just been published by the Comité des Forges. In 1913 France has produced more cast iron and steel than in the preceding years. The production of cast iron in 1913 amounted to 5,122,091 tons compared with 4,871,992 tons in 1912 and 4,426,469 tons in 1911; that is to say, an increase of 250,199 tons tons above 1912 or 5·1 per cent, and of 695,622 tons more than 1911 or 15·7 per cent. The production of raw steel amounted during the year 1913 to 4,419,241 tons against 4,078,352 tons in 1912 and 3,680,613 tons in 1911; that is to say, an increase of 341,069 tons or 8·3 per cent more than 1912, and 738,628 tons or 20 per cent more than 1911. The increase of the production, both for the cast iron and steel, is then considerable. The production of cast iron has almost doubled in the last ten years; for in 1904 not more than 2,974,000 tons were cast. The factories, having produced in 1913 5,122,091 tons of cast iron, include 156 blast-furnaces, of which at the end of the year there were 126 alight and 30 out of blast. The number of workmen occupied by the factories producing cast iron is about 15,500. As for Germany, the total production of steel in 1913 was 17,613,666 metrical tons. The number of German metallurgic factories is 244. It is thus evident that French metallurgic industry has still much to do to reach the level of the formidable German production.

LIFE WITHOUT MICROBES.

As far back as 1885 Pasteur had begun to wonder if life without microbes was possible. This problem, of the highest interest for bacteriology and biology, has remained unsolved until within the last few years. However, two years ago, in a paper presented before the Academy of Sciences by Dr. Roux, Director of the Pasteur Institute, M. Michel Cohendy showed that he had been able to bring up chickens aseptically. These experiments were much talked about at the time. At the Pasteur Institute other experimenters continued these researches. It is thus that M. Wollman succeeded in raising tadpoles and flies removed from all microbian germs, and that M. Guyenot obtained whole colonies of aseptic flies, which seems really paradoxical, seeing that flies are marvellous agents of propagation of infectious diseases. It is then actually established that animals belonging to the most diverse groups and provided naturally with a rich intestinal flora can be raised in conditions of perfect asepsy without there resulting for them any inferiority when compared with non-aseptic animals placed in observation as witnesses. As far as concerns mammals, two German savants, Nutall and Thierfelder, have shown that young guinea pigs can live perfectly and increase in weight in the absence of microbes. Unfortunately their experiments were very short. They only lasted thirteen days, and so have been open to criticism. That is why Dr. Michel Cohendy wished to extend to guinea pigs his researches on aseptic life. In a communication made to the Academy of Sciences by Dr. Roux, M. Cohendy indicates the experiments that he has been undertaking for several months past. The guinea pigs are extracted from the uterus by the cæsarian operation at a moment as near as possible to the farrowing time. They are immediately placed in an apparatus containing a provision of food, hay, clover, bran, and cakes, all perfectly sterilised. The breeding apparatus is analogous to that used for the chicken. Its structure permits of its being sterilised all at once at a temperature of 120° under pressure of steam. The different openings are shut up with cotton-wool. The air that penetrates into the interior of the cage is filtered through several filters of wadding. The water necessary for the alimentation of the guinea pigs is also sterilised. Lastly, a special apparatus enables the necessary quantity of sterilised milk to be introduced into the breeding cage. When the uterus contains two or several young ones, one or two are kept as standards for comparison. These later are raised in the same conditions of alimentation, and are as the animals that are serving for the experiments but are from their birth exposed to microbian contamination. M. Cohendy weighed the standards themselves. On the other hand, the initial weight of the animal experimented on was given by the difference in the weight of the mother before and after the extraction of the young one. In order to get a good idea of the asepsy of animals brought up in these conditions, the learned doctor, at the end of the experiment, sowed tubes of gelose with fragments of the digestive tube, of the paws, or of other organs of guinea pigs having lived separated from germs. These experiments have been clearly conclusive. M. Cohendy has made a series of nine breedings, four of which lasted sixteen, eighteen, twenty-one, and twenty-nine days. All the guinea pigs were sterile. The aseptic animals developed admirably. Their weight increased on an average from 20 to 33 per cent. On the contrary, the weight of the standards increased only from 8 to 24 per cent in the same periods. It is thus seen that it is possible to raise guinea pigs aseptically. Experiments made lately by Prof. Küster on the aseptic breeding of a young kid agree perfectly with those of Dr. Cohendy. This kid lived twelve days sheltered from all microbes; its weight increased more than that of standards. In a second experiment made by M. Küster, and which lasted thirty-five days, the weight of the young aseptic animal increased 100 per cent. These researches open a new way to the works that require the elimination of the normal microbian flora. In this way the *rôle* of the diverse species of microbes in the digestive tubes can be studied as well as the diverse microbian affections of intestinal origin, the microbian association, &c. Dr. Michel Cohendy intends to pursue his researches in a new direction.

Royal Institution.—On Tuesday next, May 19, at 3 o'clock, Prof. D'Arcy Thompson will begin a course of two lectures at the Royal Institution on "Natural History in the Classics"; and on Saturday, May 23, Prof. J. W. Gregory will deliver the first of two lectures on "Fiords and their Origin." The Friday Evening Discourse on May 22 will be delivered by Mr. Robert Mond on "The Mortuary Chapels of the Theban Nobles," and on May 29 by Prof. J. C. Bose on "Plant Autographs and their Revelations."

The Celluloid Trade.—The pamphlet "The Celluloid Trade," issued by the Fancy Goods Trade Section of the London Chamber of Commerce, makes out a very strong case against the proposed legislation relating to the storage of celluloid and articles into which celluloid enters. The memorandum calls attention to the exceedingly wide use of celluloid, and the official reports of the London Fire Brigade are quoted showing that in nine years there have been only six fires due to ordinary celluloid goods. Thus it is maintained that there is little, if any, justification for the proposed by-laws, which would be detrimental to the interests of the thousands engaged or concerned in the selling, storage, or manufacture of celluloid.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, April 30, 1914.

Sir William Crookes, O.M., President, in the Chair.

"*Presence of Inorganic Iron Compounds in the Chloroplasts of the Green Cells of Plants, considered in Relationship to Natural Photo-synthesis and the Origin of Life.*" By Prof. B. Moore, F.R.S.

"*Lack of Adaptation in the Tristichaceæ and Podestemaceæ.*" By J. C. Willis, Sc.D.

"*Genetics of Tetraploid Plants in* Primula sinensis." By R. P. Gregory.

"*Action of Certain Drugs on the Isolated Human Uterus.*" By J. A. Gunn.

"*Influence of Osmotic Pressure upon the Regeneration of* Gunda ulvæ." By D. J. Lloyd.

(*a*) "Glossina brevipalpis *as a Carrier of Trypanosome Disease in Nyasaland.* (*b*) *Trypanosome Diseases of Domestic Animals in Nyasaland.* Trypanosoma pecorum. Part III. *Development in* Glossina morsitans." By Surg.-Gen. Sir D. Bruce, F.R.S., Major A. E. Hamerton, Capt. D. P. Watson, and Lady Bruce.

"*Studies on Enzyme Action.* XXII. *Lipase.* (IV.) *The Correlation of Synthetic and Hydrolytic Activity.*" By H. E. Armstrong, F.R.S., and H. W. Gosney.

FARADAY SOCIETY.

March 27, 1914.

General Discussion on "Optical Rotatory Power."

In addition to the Papers which have already appeared the following communications were read:—

Prof. Dr. Hans Rupe (Basle) read a Paper entitled "*Some Contributions to the Knowledge of the Influence of Certain Groups on Rotatory Power.*"

The optical influence of the saturated alkyl groups is, generally speaking, an insignificant one. There are indeed some exceptions, but they nearly always have a special explanation. We are, on the whole, able to point out their influence as the normal one.

But "the presence of unsaturation leads to an irregularity." The combination of two pairs of double bonds which Thiele calls "conjugated" sometimes has a strong influence on the optical rotation, but when certain radicals, as the CH_3 or the C_6H_5 group, are combined with the central carbon atoms we observe that this strong increasing effect vanishes entirely.

Very curious is the effect of the *phenyl* group on rotatory power and not easy to analyse. Close to the asymmetric carbon it nearly always increases the optical rotation. But here already we find some exceptions; thus the benzoyl ester of carvoxime has a lower rotation than the derivative of phenylacetic or phenylpropionic acid. As the phenyl group is displaced away from the asymmetric carbon atom, its positive effect diminishes until it becomes less than that of an alkyl group; finally the effect may even become negative. The positive influence of the phenyl group is a polar one depending on its electro-negative character, but what is the negative influence?

The most interesting part of the chemistry of conjugation is due to the combination of the double linking with one or two phenyl groups. This combination can produce a very powerful increasing influence on the rotatory power, particularly when it is near the asymmetric carbon, and a great amount of work is done on this subject. Rather similar also is the effect of a combination of the C:O group with a phenyl nucleus or a carboxyl group pointed out by Hilditch. But the author is not of Hilditch's opinion that the degree of conjugation is here the principal thing and not the distance; he demonstrates by several examples how important is the distance for the influence of a conjugation.

Very particular is the influence of a combination which the author calls accumulation of unsaturated groups, as, for instance, a double linking combined with a phenyl and a carboxyl or two phenyl groups. The rule here is, that such an accumulation has a depressing influence on rotatory power; very seldom only we find the opposite effect.

The author has not been able hitherto to find any satisfactory explanation for both effects of the unsaturated complexes—the increasing and the depressing one. Neither the fact that several unsaturated groups contain more energy than the saturated ones nor the fact that the molecular volume of the unsaturated groups is greater than that of the saturated is a sufficient explanation. The author has also been unsuccessful in his attempts to find an explanation by using the theory of Stark-Kaufmann of the valency-electrons.

The author finally discusses the question of whether optical rotation may be of service in helping to determine the constitution of optically active organic compounds.

Prof. Dr. H. Grossman (Berlin) read a Paper entitled "*Studies in the Rotatory Dispersion of Tartaric Acid and Malic Acid.*"

The phenomenon of so-called anomalous rotatory dispersion, which was first observed in aqueous solutions of tartaric and malic acids, has called forth numerous theories. The early investigations of the influence of organic solvents on the neutral esters of malic and tartaric acids had, however, shown that these apparently exceptional phenomena are frequent, and that they occur always in the neighbourhood of the zero point, *i.e.*, apparently together with optical inactivity, as soon as materials which call forth a tendency to a reversal of the rotation are added to the pure optically-active substance. This tendency to a reversal in the sign of the rotation was traced back to the formation of more or less stable addition-compounds. In the case of the two acids the relations are complicated by the ionisation. Organic solvents which impede the ionisation of the two acids more than water does will therefore resemble in their behaviour more the concentrated aqueous solutions than the diluted solutions or the solutions of the neutral salts. In the two latter instances the rotation increases normally, for tartaric acid and its salts, from the red to the violet end of the spectrum, but an addition of an organic solvent results in general in a diminution of the dextro-rotation, which may become sufficiently strong to produce a lævo-rotatory system. In such cases the sense of the dispersion, which increases to the left of the zero point from the red to the violet in a negative sense, is likewise reversed. The malic acid offers quite analogous relations, in the opposite sense, however. In that case also we observe anomalous rotatory dispersion with a pronounced maximum in the yellow, green, and blue near the zero, at which we must assume the existence of at least two optically-active systems of different rotatory dispersions. The justification of this view is strongly supported by the behaviour of tartaric and malic acids towards concentrated sulphuric acid and phosphoric acid. Of otherwise remarkable results concerning the influence of organic solvents on the rotation of malic acid in particular we accentuate the occurrence of muta-rotation when malic acid is dissolved in benzylalcohol and in mixtures of benzylalcohol, pyridin, and formic acid; the last-mentioned acid displays the same phenomenon when acting as solvent for tartaric acid.

The investigations clearly demonstrate that the observation of the rotatory dispersion always admits of much more reliable conclusions as to the existence of labile addition-compounds in solution than determinations with mono-achromatic light could lead to.

Papers contributed to the discussion by M. G. Bruhat (Paris), Dr. E. Darmois (Paris), and Prof. A. Cotton (Paris) were communicated by Dr. H. Borns.

M. Bruhat's Paper was on "*The Rotatory Power of Tartaric Acid.*"

The diverse anomalies which are seen in the variation of the rotatory power of tartaric acid with the wave-length, the nature of the solvent, and the concentration cannot be explained by the existence of an absorption band in the ultra-violet, nor by a purely physical effect of the solvent. They can, however, be accounted for if we assume that there exist in the solutions two active compounds which are in equilibrium with one another, in proportions which vary with the nature of the solvent, the concentration, and the temperature. The author has measured the rotatory dispersion, at different temperatures, of superfused tartaric acid in the absence of any solvent. He shows that the dispersion curves approach the curves for solutions of different concentrations; rise of temperature acts like a dilution, augmenting the rotatory power, displacing the maximum towards the violet, and finally rendering the dispersion normal. The two compounds in equilibrium are therefore tartaric acid itself and a polymer; cryometric observations indicate that the proportion of this latter must be small and its rotatory power high.

Dr. Darmois's paper was on "*The Existence of Racemic Tartaric Acid in Solution.*"

The rotatory power and the rotatory dispersion of dextro-tartaric acid, in aqueous solution, depend on the concentration. In diluted solutions the rotatory power is strong and the dispersion is normal. In concentrated solutions the rotatory power is feeble and the dispersion is anomalous. The object of the research is to study mixtures, *in different proportions*, of the dextro-acid and the lævo acid.

The concentration of the solution is chosen so that the concentration *of total acid* is high and the *excess* of the one acid (*e.g.*, the dextro-acid) is small. If racemic acid exists in the solution, its rotatory power is nil; the dispersion should be equal to that due to the acid in the excess (*i.e.*, normal). If, on the other hand, racemic acid does not exist in solution, the rotatory power should be that of a mixture of the two acids (dextro and lævo); the dispersion should be that of a concentrated solution (*i.e.*, anomalous).

The experiments justify the second hypothesis. The solution behaves like a mixture of dextro-acid and lævo-acid.

Further, if we mix racemic acid and dextro-tartaric acid, the solution behaves like a mixture of the dextro-acid and the lævo-acid. The solution behaves in every respect as if the racemic acid were dissociated into its two constituents.

Prof. Cotton's paper dealt with "*The Constitution of Liquid Mixtures and Rotatory Power.*"

A question of particular importance in physical chemistry may be put as follows:—What happens when we mix two pure liquids? One of the theories which have been advanced for the purpose of explaining the properties of these mixtures, such as are not merely additive, may be called a "chemical" theory. This theory assumes that there exist, in the mixture of the two bodies A, A', by the side of molecules of A and of molecules of A', *mixed complexes of definite composition*. A variant of this theory assumes that there are in the mixture, in addition to the molecules of the two pure substances, also *associations* AA, which only contain molecules of one kind and whose number varies with the dilution.

In conjunction with H. Mouton the author proposes certain methods of submitting this chemical theory to the experimental test. The first method is based upon the researches of Darmois. The author gives a generalised account of Darmois's considerations, and shows that the magnetic birefraction can, in the application of this method, replace the rotatory power. In either case measurements are made with *several* monochromatic radiations. The second method consists in measuring successively, in mixtures of diverse concentrations, both the rotatory power and the magnetic birefraction; in this case we may limit ourselves to making use of one radiation only. We may investigate, either mixtures containing a body A endowed with both rotatory power and magnetic birefraction, and another body A', inactive and not birefracting; or mixtures containing a body A endowed with rotatory power only, and another substance A' which is only birefracting. This latter case affords more complete information and enables us to distinguish the mixed complexes from the associations.

The simplification which is attained in the problem of the constitution of mixtures by the consideration of the rotatory power (or of the birefraction) is due to the fact that in both these cases we know diluents which are in themselves *inactive*.

Discussion.

The discussion hinged very largely on the nature and causes of anomalous rotatory dispersion. There is some doubt as to the exact meaning that should be attached to this term, but speaking generally it may be said that rotatory dispersion is regarded as *normal* when the rotation increases steadily with decreasing wave-length, and as *anomalous* if in any part of the spectrum it diminishes with the wave-length.

Dr. Patterson protested against the artificial character of this distinction, since a curve which was "normal" in one part of the spectrum might easily become "anomalous" in another part of the spectrum. Again, the curves of rotatory dispersion for a substance like methyl tartrate belonged obviously to one family and differed mainly in the position of the maximum rotation. If this fell in the visible part of the spectrum the curves were described as anomalous, but surely they were equally anomalous if the maximum were displaced into the ultra-violet or into the infra-red.

Dr. Lowry and Mr. Dickson agreed with this criticism and urged that the only logical distinction was between the *simple rotatory dispersion* of compounds which obeyed the law $\alpha = \frac{k_0}{\lambda^2 - \lambda_0^2}$ and the *complex rotatory dispersion* of compounds which required two or more of these terms. It was impossible to tell by the eye whether a curve was simple or complex, but this point could be tested very easily by plotting $1/\alpha$ against λ^2, when the points would be found to fall on a straight line if the dispersion were simple, but on a curve if the rotation were complex.

As regards the origin of anomalous rotatory dispersion, Prof. Frankland and Dr. Patterson both urged that anomalous rotatory dispersion could be accounted for by the drift of the temperature-rotation curves. If these intersected in a point the dispersion might be normal under all conditions; if, however, they intersected over a range of temperatures the dispersion would be anomalous over this range.

Dr. Lowry, in reply, maintained that the dispersion curves were fundamental, whilst the secondary curves were secondary. In measuring rotatory dispersion nothing was changed except the nature of the light which was used to test the properties of the substance; when the temperature was changed the chemical character of the liquid might be completely altered owing to the dissociation of complex molecules, and in the case of solutions by the breaking down of compounds of solvent and solute. In cases of simple rotatory dispersion the temperature rotation curves would intersect on the axis of zero rotation; for the whole spectrum to give an equal rotation other than zero would be nothing less than a miracle. In cases of complex rotatory dispersion the temperature curves would naturally intersect over a range of temperatures, but this would be a secondary effect and not the cause of anomalous dispersion.

The view that anomalous dispersion is due to the presence of two or more kinds of optically active molecules was upheld by Prof. Armstrong, who urged the possibility of dynamic isomerism; by Prof. Grossman, who postu-

lated compounds of solvent and solute; by Dr. Pickard and Mr. Kenyon, who had detected anomalous dispersion in naphthyl methyl carbinol, $C_{10}H_7 \cdot CH(OH) \cdot CH_3$, and thought it might contain two isodynamic forms of the aromatic nucleus; by Dr. A. McKenzie, who suggested that polymeric forms of tartaric acid might exist (a view also advocated in M. Bruhat's paper on the rotatory power of fused tartaric acid); and by Dr. Lowry, who stated in the discussion that nitro-camphor, which is known as an example of dynamic isomerism, also exhibits anomalous rotatory dispersion, and that ethyl tartrate, a typical example of a substance having anomalous dispersion, can be fractionated into portions which differ widely in their rotatory power for violet light.

Whilst attention was largely directed to the new developments introduced by the measurements of rotatory dispersion, Prof. Frankland and Dr. McKenzie had no difficulties in showing the very valuable results which have been obtained from experiments made with light of only one wave-length. If proof were needed, Prof. Rupe's paper would have been sufficient refutation of any suggestion to the contrary effect.

NOTICES OF BOOKS.

Intermetallic Compounds. By Cecil H. Desch, D.Sc., Ph.D., F.I.C. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1914.

The author's wide knowledge of metallography and his marked power of clear explanation have enabled him to produce a valuable monograph on the formation of intermetallic compounds. The literature of the subject contains a large number of unsubstantiated facts, and it requires a sound critical judgment to sift the actual truth from them, as the author has done with great success. The method of thermal analysis is first discussed, and some notes are added upon the microscopical control of the results obtained by its application. The difficulties attending the isolation of metallic compounds are described, and then the physical properties of the compounds are treated, emphasis being laid upon the relations between each individual property and the composition. The attempts which have been made to formulate a theory of the constitution of intermetallic compounds are discussed, and suggestions are made as to lines of research which may prove fruitful. No practical methods of investigation are described, but the monograph gives a very fair and unbiassed view of the present state of our knowledge of the theory of this branch of metallography.

Industrial Chemistry for Engineering Students. By Henry K. Benson, Ph.D. New York: The Macmillan Company. 1913.

This book will be found useful for engineering students who have been through elementary courses in pure chemistry and physics, and wish to study the applications of scientific principles to industrial problems, and to acquire some knowledge of the chemistry of the materials and processes which are of special importance from an engineering point of view. The subjects treated in particular include fuels, clay products, cements, &c., while water, industrial alloys, paints, paving materials are discussed rather less fully. The author appears to have selected his material carefully with a view to its general utility, and although American products and practice are naturally given the chief prominence the book may find useful application in English technical schools. The full bibliographies given at the end of each chapter have been very carefully compiled, and will be of great practical value to chemists and engineers.

A Text-book of Physics. Electricity and Magnetism. Parts I. and II. By J. H. Poynting, Sc.D., F.R.S., and Sir J. J. Thomson, O.M., M.A., F.R.S. London: Charles Griffin and Co., Ltd. 1914.

This volume contains Parts I. and II. of the fourth book of the authors' text-book of physics, and deals with static electricity and magnetism. It is in every respect fully up to the level of the earlier volumes on the Properties of Matter, Sound, and Heat, and no higher praise can be given to it. The authors have written for those who have no previous knowledge of electricity or magnetism, and teachers of physics and college students will appreciate the exceedingly clear style in which the book is written. This is particularly noticeable in the chapters devoted to the discussion of propositions applying to "inverse square" systems and to stresses in the dielectric. Both in the descriptions of experiments and the working out of mathematical formulæ the authors smooth the path of their readers as much as possible, making the subject intensely interesting and at the same time providing a firm foundation for the study of more detailed and advanced works.

Kapillarchemie und Physiologie. ("Capillary Chemistry and Physiology"). By Dr. H. Freundlich. Second Edition. Dresden and Leipzig: Theodor Steinkopff. 1914. (Mk. 1.50).

The text of this lecture has been only very slightly altered in the second edition, but recent work has been summarised in an appendix, in which descriptions are to be found of many experimental confirmations of the author's views. The essential features of adsorption phenomena are very shortly discussed, and their importance in physiology is explained, and workers in biochemistry will find that the lecture gives them a readable outline of some aspects of physiological problems. The author has made it clear in the appendix that in some matters of detail his opinions have undergone a certain amount of alteration, and his view of the phenomena is, on the whole, unbiassed.

Les Origines Mystiques de la Science "Allemande"). ("The Mystical Origins of 'German' Science") By René Loti. Paris: Félix Alcan.

This thesis discusses, from a point of view which can hardly be described as free from partisanship, the errors which have been introduced into science by mysticism, and the revival of what may be called a modern variety of mysticism in Germany. For those who are interested in the philosophy of science the monograph will be found to give a detailed account of certain points of view, and the author has evidently searched many sources for his material.

Die Theorie der Strahlung und der Quanten. ("The Theory of Radiation and Quanta"). Transactions of the Solvay Conference, 1911. Translated into German by A. Eucken. Halle-a.-S.; Wilhelm Knapp. 1914. (Mk. 15.60).

The papers read at the Conference held at the suggestion of Prof. Solvay in the autumn of 1911 in Brussels are printed in full in this report together with the discussions that followed them. Unavoidable circumstances have delayed the publication of the report, but in essentials the quanta theory has seen only very slight modifications during the last two years, and its development in matters of detail has been traced down to the end of 1913 in an appendix. The conference was attended by some of the world's leading physicists, and papers were contributed by, among others, Lorentz, Jeans, Planck, Perrin, and Nernst. In the discussions some very interesting points were raised, and physicists will be glad to have so clear and detailed an exposition of the most modern aspects of the quanta theory.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clviii., No. 13, March 30, 1914.

Basic Carbonates of Copper.—V. Auger.—The amorphous basic carbonate of copper, $8CuO.5CO_2.7H_2O$, the composition of which is very nearly that of a hydrated azurite, is transformed, even in presence of CO_2 under 40 atmospheres, into hydrated malachite with loss of CO_2, but if these substances are kept under pressures above 3 or 4 atmospheres the transformation into azurite takes a period of time which varies, according to the pressure, from some days to some months. On the other hand, the transformation into azurite is very rapid if a small quantity of azurite is added to start the reaction. Azurite can be obtained rapidly and in large quantity if small portions of a soluble salt of copper are added to a solution of $Na_2CO_3+NaHCO_3$ containing azurite in suspension. The double salt, $CuNa_2(CO_3)_2 3H_2O$, when subjected in presence of a little water to the action of CO_2 under a pressure of 40 atmospheres, gives, after a few days, a mixture of azurite and $NaHCO_3$. The anhydrous salt, $CuNa_2(CO_3)_2$, can be obtained by heating on the water-bath a very concentrated solution of $Na_2CO_3+NaHCO_3$, saturated with the hydrated salt.

Heats of Formation and other Properties of Alkaline Protosulphides.—E. Rengade and N. Costeanu.—The absolute densities of the alkaline sulphides at the temperature of the laboratory are:—Na_2S, 1·856; K_2S, 1·805; Rb_2S, 2·912. The heats of solution are:—

Na_2S sol. + H_2O = Na_2S diss. .. .. +15·5 cal.
K_2S sol. + H_2O = K_2S diss. .. .. +22·7 cal.
Rb_2S sol. + H_2O = Rb_2S diss. .. .. +24·6 cal.

These numbers increase regularly with the atomic weight. The heats of formation are:—

Na_2 sol. + S sol. = Na_2S sol. .. .. +89·7 cal.
K_2 sol. + S sol. = K_2S sol... .. .. +87·1 cal.
Rb_2 sol. + S sol. = Rb_2S sol. .. .. +87·1 cal.

The heats of formation decrease with the atomic weight. The equality of the two last results is fortuitous. The three sulphides are not isomorphous.

Precipitation of Alumina in presence of Fluorides.—H. Cavaignac.—When alumina is determined in presence of hydrofluoric acid the acid is incompletely eliminated even after repeated heating with sulphuric acid; the precipitation with ammonia is thus incomplete, more so when the solution is heated than in the cold.

Salicylic Nitriles.—MM. Cousin and Volmar.—Three different substances have been described under the name of salicylic nitrile or *o*-cyanphenol:—(i.) The true nitrile, $C_6H_4<^{OH(1)}_{CN(2)}$, fusing at 98°. (ii.) A substance fusing at 195°, prepared by Grimaux by dehydrating salicylamide with phosphoric anhydride. (iii.) A substance fusing at 300°, isolated by Limpricht, and regarded by Grimaux as a polynitrile. The authors have proved that the substance fusing at about 200° is identical with disalicylamide, while Grimaux's polynitrile is really a trioxytriphenyltriazine, which can be converted into a trioxytriphenylglyoxaline of mpirical formula $C_{21}H_{16}O_3N_2$.

Atti della Reale Accademia dei Lincei. Vol. xxiii. [i.], No. 4, 1914.

Behaviour of Boric Ethers with Alcoholates.—Livio Cambi.—By acting with boric ethers on solutions of alcoholates the author has prepared the boron-oxymethyl salts of sodium, lithium, potassium, and calcium; the boron-oxyethyl salts of sodium, potassium, thallium (thallous), and the boron-oxypropyl salt of sodium. The study of the properties of these substances shows that they frequently contain alcohol of crystallisation, and in the majority of cases there is not a whole number of molecules of alcohol of crystallisation to one molecule of salt. The compounds are stable, and behave like true salts.

MISCELLANEOUS.

Royal Society.—At the meeting on May 7, 1914, the following candidates were elected Fellows of the Royal Society:—E. J. Allen, R. Assheton, G. T. Bennett, R. H. Biffen, A. E. Boycott, C. Cuthbertson, D. H. Dale, A. S. Eddington, E. J. Garwood, H. H. Havelock, T. M. Lowry, D. N. Paton, S. Ruhemann, S. W. J. Smith, T. E. Stanton.

Royal Institution.—A General Meeting of the Members of the Royal Institution was held on the 4th inst.; Sir James Crichton-Browne, Treasurer and Vice-President, in the Chair. Sir John H. Biles, Mr. R. C. Bussell, Mr. J. Carmichael, Mr. R. L. Cookson, Mr. M. S. Napier, and Miss K. O'Sullivan were elected Members. The Chairman announced that a legacy of £100 had been received from the Executors of the late Mrs. Singleton. The special thanks of the Members were returned to Mr. R. Pearce for his donation of £100 to the Fund for the Promotion of Experimental Research.

MEETINGS FOR THE WEEK.

Tuesday, 19th.—Royal Institution, 3. "Natural History in the Classics," by Prof. D'Arcy W. Thompson, C.B.
—— Royal Society of Arts, 4.30. (Cobb Lecture). "The Singing of Songs, Old and New," by H. Plunket Greene.

Wednesday, 20th.—Royal Society of Arts, 8.30. "The Channel Tunnel and its Early History," by J. C. Hawkshaw.
—— Microscopical, 8. Exhibition of Microscopic Aquatic Life.

Thursday, 21st.—Royal Institution, 3. "Identity of Laws, in General and Biological Chemistry," by Prof. Svante Arrhenius, D.Sc., &c.
—— Royal Society of Arts, 4.30. "The Indian Census of 1911—Ethnography and Occupations," by E. A. Gait.
—— Royal Society. "Effect of the Magneton in the Scattering of α-Rays," by W. M. Hicks. "Luminous Vapours Distilled from the Arc, with Application to the Study of Spectrum Series and their Origin," by Hon. R. J. Strutt. "Ionisation of Gases by Collision and the Ionising Potential for Positive Ions and Negative Corpuscles," by W. T. Pawlow. "Determination of Elastic Limits under Alternating Stress Conditions," by C. E. Stromeyer. "Emission of Electricity from various Substances at High Temperatures," by G. W. C. Kaye and W. F. Higgins.
—— Chemical, 8.30. "Ionisation and the Law of Mass Action — Part III., Utilisation of the Osmotic Data and a New Dilution Law," by W. R. Bousfield. "Influence of Nitro-groups on the Reactivity of Substituents in the Benzene Nucleus," by J. Kenner. "Some Indazole Derivatives," by R. Curtis and J. Kenner. "Viscosity of Sugar Solutions," by H. Green. "Compounds of Phenanthraquinone with Metallic Salts," by J. Knox and H. R. Innes. "Quinone-ammonium Derivatives — Part III., Dihaloid, Monoazo-, Bisazo-, Nitrotriazo-, and Bistriazo-compounds—Attempts to prepare Derivatives containing an Asymmetric Quinquivalent Nitrogen Atom," by R. Meldola and W. F. Hollely.

Friday, 22nd.—Royal Institution, 9. "The Mortuary Chapels of the Theban Nobles," by Robert Mond, M.A., &c.
—— Physical, 5. "Volatility of Thorium Active Deposit," by T. Barratt and A. B. Wood. "Passage of α-Particles through Photographic Films," by H. P. Walmsley and W. Makower. "Null Method of Testing Vibration Galvanometers," by S. Butterworth. "Experiments with an Incandescent Lamp," by C. W. S. Crawley and S. W. J. Smith.

Saturday, 23rd.—Royal Institution, 3. "Fiords and their Origin," by Prof. J. W. Gregory, F.R.S., &c.

THE CHEMICAL NEWS.

VOL. CIX., No. 2843.

RADIO-ATOMS: THEIR ATOMIC WEIGHTS AND VALENCIES.

By F. H. LORING.

IT seems probable that the radio-elements are made up of associate atoms differing in atomic weight, and that they are exactly whole numbers taken from a Rydberg atomic-weight series (see CHEM. NEWS, cix., 169).

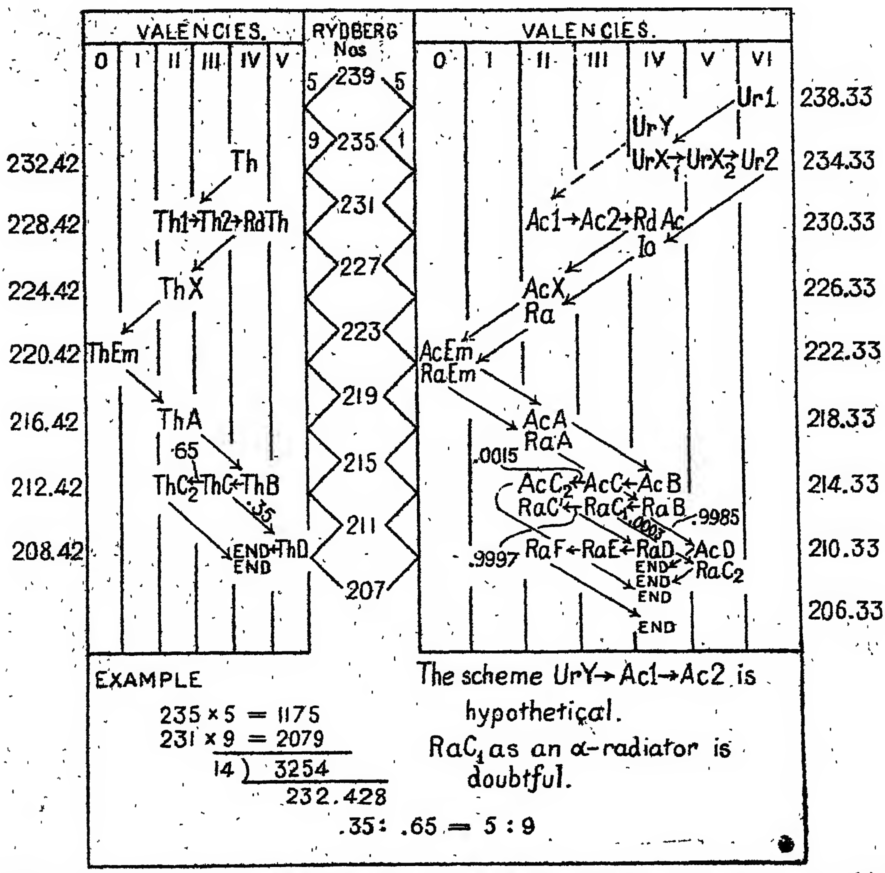
The branching in the thorium series at thorium C suggests the possibility that, at this point, the associates virtually part company, and that the respective end-products may be considered as consisting of homogeneous whole-number atomic-weight atoms, standing in proportionate numbers to each other in the same ratio as the products thorium D and thorium C_2, namely, 0·35 : 0·65 per cent, *i.e*, as 5 to 9. Then thorium itself should be a mixture: $Th^{II}235_5 + Th^{I}231_9$. The mean value is 232·428, which is in agreement with the present accepted value for thorium, namely 232·42.

Assuming, therefore, for example, that thorium emanation has associates of atomic weights 223 and 219 in the above proportion, then it seems probable that the radium and actinium emanations are also made up from exactly the same Rydberg numbers, but in a different proportion.

Hönigschmid (*Acad. der Wiss. Wien.*, Jan. 22, 1914), in a recent determination of the atomic weight of uranium, gets the value 238·175, which seems too low, as the present accepted value is 238·5 (Richards). A mean between these two values would be 238·33, which is close to a mean of six variable measurements by Œ. de Coninck (*Comptes Rendus*, 1912, clv., 1511), namely, 238·4.

Taking, therefore, the value 238·33 as a probable one the ratio of the associates would be 1 : 5. Moreover, if the values be of the right order, then the products should probably lie in approximate alignment when tabulated, so that, for example, RaEm, ThEm, and AcEm are in the same horizontal zone, apart from their valence-position.

The accompanying table shows the atomic weights,



In the table, each long arrow represents the loss of an α-particle (one helium atom carrying two positive charges of electricity), and each short arrow represents either the loss of one β-particle (one negative electron) or an apparent rayless change. Since the table is crowded where the different members fall together, it should be noted that the end-products according to this scheme have the following atom-weights and relative atom-numbers:—

Th-end 207_9; Ra-end^{II} 207_1; Ac-end 207_1; Ra-end^{I} 203_1;

Th-end 211_5; Ac-end^{II} 211_5; Ac-end^{II} 211 ; Ra-end^{II} 207_5.

The last two sets (taken vertically) in mean are 210·33 and 206·33 respectively. The exceedingly small quantity of RaC_2 formed renders the α-rays of the RaC_1 difficult to observe: no α-rays have been detected.

valencies, &c., as the result of this study. Mesothorium 1 and mesothorium 2 are abbreviated respectively: Th_1, Th_2.

It will be seen that the valence-positions of the radio-elements are in accordance with the experimental determinations of valency, being, in fact, a modified form of the Russell-Fajans-Soddy classification, based on the experimental work of G. von Hevesey, Fleck, and others.* It is to be noted that uranium Y is placed in the same atomic-weight and valence-position as uranium X_1. These elements are supposed to be isotopic (see Soddy, *Phil. Mag.*, 1914, xxvii., 215). Uranium Y arises either from uranium 1, taking its place with uranium X_1, or from uranium 2, taking its place with ionium; but uranium Y has not yet been found to give α-rays, so its position with reference to actinium is uncertain. Actinium 1 is, of course, hypothetical. Ac_2 = actinium.

The probable fact that the thorium series is made up of associate atoms differing in atomic weight, which do not become apparent until a species of dissociation sets in towards the end of the transformation process, implies, by analogy, that the equivalent in the right-hand group would be the re-union of the radium and actinium families from, say, uranium Y downwards. If such be the case, then actinium emanation would consist wholly of atoms of atomic weight 223, whilst radium emanation would be equally homogeneous, consisting of atoms of atomic weight 219 each.

This can hardly be the case, as the very small number of atoms (relative to the whole) from one branch product, radium C_1 (= 0·0003 per cent), is one-fifth of the number from the other, actinium C (= 0·0015 per cent), suggesting that these are homogeneous separations like that assumed at thorium C, but not carried out to anything like completion as in the thorium series.

Moreover, Hönigschmid's value for the atomic weight of radium, 225·97, is against the idea which would assign a value of 223 or 227 to this element. It is worth remarking in this connection that 226 is *not* a Rydberg number. The Curie-Ramsay value, 226·4, is also favourable to the former view.

Prof. Soddy has pointed out that the 6 end-products are probably isotopic, and may represent the composite element, lead, which has a mean atomic weight of 207·10.

Taking into account the relative percentages of the products, both in the three main series and at the C-branches, the summation in mean of all the end-products yields the atomic weight value 207.

Commenting on the genesis of the elements, the well-known pendulum conception, due to Crookes, is reasonable when rightly interpreted, since the energy stored in the atom has doubtless an origin in some great cosmic process, and there is no reason why a few atoms, overcharged as it were, cannot give up their energy and thus reveal the original process, or rather continue the process far enough to simulate the recoil of the final swing of the pendulum, although the state represented by the oscillating pendulum has long since ceased to exist.

I think, therefore, that the complexity of lead might be considered, in a sense, accidental, since the process of element-formation at the end of the Periodic series has over-reached itself, and, by a reflex action, as if by an irregular backward final slump or recession of the pendulum, has laid down a group of elements that happen to synchronise, or "slump together" at lead; consequently, it would not be a correct extension of the process to carry the complexity of lead down through the entire Periodic Table. Probably, however, many of the elements have a complexity like that of thorium. In fact, if the above analysis be correct, the inference is undoubtedly that the common elements have *two* types of atoms in many cases, but not necessarily *more* as in the case of lead.

April 15, 1914.

* In the Jan., 1914, issue of *Le Radium*, the valencies of practically all the radio-elements except UrY, UrX_2, RaC_2, RaC′, AcC_2, AcD, ThD, and ThC_2 are tabulated. The valencies above given are in agreement with these valencies, except in the case of the B-members and RaD, which are indicated as divalent instead of tetravalent, as here shown. The idea of assinging what might be termed complementary valencies to the lower half of the table suggests itself, in which case the values 0—1—2—1—2—3—2, or [8]—7—6—5—5—3—2, may be considered in the light of experiment. By assigning the latter numbers to the lower half of the table, the entire classification agrees with Soddy's group-numbers for the radio-elements.

DRY AND WET STRENGTHS OF PAPER AND PAPER YARNS.

By CLAYTON BEADLE and HENRY P. STEVENS.

As far as we know, attempts to determine wet strength of paper have been confined almost entirely, if not wholly, to paper merely in a damp condition; that is, with a limited amount of moisture such as would be imparted to paper by placing it between damp cloths or in atmospheres more or less saturated with moisture, and tests have been made showing the variation in strength of paper in comparison with the amount of moisture which it retains under such circumstances.

Also numerous tests have been made showing the relationship of strength and degree of atmospheric saturation with that of the hygroscopic moisture in the papers of different compositions. These latter determinations have led to the unanimous conclusion by all observers that there is a certain percentage of hygroscopic moisture for all papers (which is a somewhat variable figure according to the nature of the material) at which a maximum strength is obtained. This condition is perhaps arrived in an ordinary medium room temperature between 70 and 80 per cent atmospheric saturation.

Ninety-nine per cent of the paper produced for ordinary commercial purposes has no strength whatever after immersion in water; that is, with such papers there is not sufficient strength to indicate anything on a testing machine. Therefore the strength of a paper after immersion in water, for obvious reasons, has not been investigated. There is no strength in most papers after prolonged immersion in water, even when rosin sized or gelatin sized; but a paper can be made to possess strength even on water immersion if gelatin sized and subsequently treated with formalin to render the gelatin insoluble. Vegetable parchment, which is produced by passing a water-leaf paper through sulphuric acid and subsequent washing and drying, is also a form of paper which possesses some considerable wet strength. There are other papers, such as photographic paper, which require to have some strength on immersion in water; such papers are prepared by special processes. But in the ordinary course of manufacture it is only in the domain of very strong paper that we can look for any appreciable strength on immersion. In passing, we should not forget the importance of high wet strength for many kinds of bag and wrapping paper used for goods which are either moist or require protection from moisture.

There is one kind of paper now coming into extensive use where wet strength would be a most welcome quality, namely, that used in the manufacture of paper yarns.

Table I. shows tests on papers as at present used for paper yarns.

TABLE I.—*Test on Papers as at present Used for Paper Yarns*

Papers.	Tested.	Substance in grms., per square metre.	Breaking strain, in grms., per inch wide.	Breaking length, in kilometres.
Brown Kraft	Dry	49	9035	8·42
	Dry	41	9950	9·70
	Wet	41	0	0
Yellow Kraft	Dry	44	9850	9·60
	Wet	44	635	0·58

The figures given in this and subsequent tables are the average of ten independent tests. These are the very

TABLE II.—*Tests on Paper Yarns now on the Market.*

Paper.	Tested.	Width of strip. Mm.	Weight, in grms., per metre length.	Number of twists per metre.	Breaking strain, in grms.	Breaking length, in kilometres.	Relative strength when highest = 100.	Diminution in strength as the result of wetting Per cent.
Swedish Kraft ..	Dry	7	0·200	350	1278	6·40	77	
	Wet	7	0·200	350	940	4·70	56	27
Swedish Kraft ..	Dry	7	0·470	450	2189	4·66	56	
	Wet	7	0·470	450	1976	4·20	50	10
Swedish Kraft ..	Dry	6	0·250	400	2081	8·33	100	
	Wet	6	0·250	400	1135	4·55	55	45
Swedish Kraft ..	Dry	4	0·195	200	1590	8·16	98	
	Wet	4	0·195	200	635	3·26	40	59

strongest papers obtainable. In the dry state they possess a breaking length in the neighbourhood of 10 kilometres, but it will be observed that one of the papers has a breaking length of 0 and the other a breaking length which is only about 6 per cent of that of the dry paper.

When paper is twisted, as in the case of paper yarn, the properties as regards wet strength after immersion are altered. If a piece of paper yarn cloth is immersed in water, say, for twenty-four hours and examined, it will be found that it has very considerable strength. In fact, from a hand examination it appears as strong after immersion. As regards its behaviour under water, it would almost appear that the yarn was made from natural fibres. If now a piece of the yarn is stripped from a closely woven paper yarn fabric and pulled, it would be observed that it has some considerable wet strength, but not so much as might be inferred from the general handling of the wet fabric. Untwist the yarn when it will be noticed that the strip of paper comes apart without any exertion whatever; in other words, the wet strength of a paper yarn cloth is not due to the wet strength of the paper from which it was produced but from the fact that the fibres of the paper are twisted, and the twisted yarn is then woven. The paper yarn cloth on immersion has no cohesion among the fibres in the sense that that paper has that has lost its felting qualities as it is understood by paper makers, and although the average length of the fibres may be 1·0 mm. the paper yarn cloth depends almost entirely for its wet strength upon the peculiar juxtaposition of these short fibres as the result of (*a*) the way they have been disposed when in course of felting together upon the wire of the paper machine; (*b*) the twisting of the strip; (*c*) the weaving. These combined agents result in the formation of a textile product the length of the ultimate fibre of which must be exceedingly small in comparison with that of most textile products. Directly the fibres of the paper are placed more or less parallel by the untwisting of the yarn then the wet strength becomes practically nil.

Table II. gives particulars of paper yarns tested, both dry and wet. They are all produced from Swedish krafts. The width of the strip and the weight of the yarn per metre is given, as well as the twists per metre. Also the actual breaking strain of the yarn in grms., which is calculated to breaking length in kilometres, and, for purposes of comparison, the relative breaking lengths are given with the highest at 100, and in a final column the diminution in a strength as the result of wetting.

It will be observed that the wet strength is at least half the dry strength—in fact, on an average about two-thirds the dry strength, whereas the paper from which these yarns are produced (Table I.) the highest wet strength is only 6 per cent, or less than one-fifteenth part of the dry strength.

The chief object of this investigation was to determine the qualities of Hedychium paper for its suitability for paper yarn. Table III. gives figures for paper yarns made from Hedychium paper. The Hedychium paper was produced on a paper machine under our direction. The paper had a substance of 42·5 grms. per square metre and possessed parchment-like and self-sizing qualities. The breaking length of the paper in the direction of the web was 10·03 kilometres—rather greater than that of the strongest Swedish kraft, but, unlike the Swedish kraft, it possesses considerable wet strength after prolonged immersion. The wet strength of this paper was 1·58 kilometres.

TABLE III.

	Tested.	Width of strip.	Weight of yarn, in grms., per metre.	Breaking strain of yarn, in grms.	Breaking length of yarn in, kilometres.
Hedychium yarn made by Beadle and Stevens in London	Dry	6	0·289	2210	7·65
	Wet	6	0·289	1415	4·90
Hedychium yarn made on German machine..	Dry		0·264	1883	7·13

It will be observed, on comparing the above figures for the Hedychium paper with those of Hedychium paper yarn produced therefrom, that the yarn has diminished in dry strength by about 34 per cent, if the first of the yarns is taken, but has very much increased in wet strength as the result of the twisting. Thus the wet strength of the Hedychium paper at 15 per cent of its dry strength and the Hedychium yarn produced therefrom is 64 per cent. We have already shown that many fibro-vascular bundles and natural fibres, on prolonged immersion in water, lose quite as much as this when tested for wet strength, but of course such fibres are tested in an untwisted condition.

TABLE IV.—*Hedychium Yarns produced by Spinning from Undried Paper directly after Couching.*

Time of beating. Hours.	Tested.	Weight of yarn, in grms. per metre.	Breaking length, in metres.	Relative breaking length when highest = 100.	Loss of strength due to wetting. Per cent.
3	Dry	0·415	3·66	76	
3	Wet	0·415	2·05	43	44
3½	Dry	0·370	4·73	99	
3½	Wet	0·370	2·12	44	55
4	Dry	0·400	4·80	100	
4	Wet	0·400	1·79	38	62

Comparing the above Hedychium yarn figures with yarns produced from Swedish kraft, it will be noticed in the latter that the average diminution in strength from dry to wet is about the same, namely, 36 per cent. The actual dry breaking length of Hedychium yarn (average, Table III.) is 7·37 kilometres, and the average of the Swedish kraft yarn is 6·89 kilometres (Table II.). Thus, already, although we have only reached the initial stages of Hedychium yarns, a better result has been obtained from Hedychium than has been obtained from the best Swedish kraft. As the Hedychium paper from which the yarns were produced had a breaking length of 10·03 kilometres the Hedychium yarn has about 73 per cent the strength of the paper, and a somewhat similar diminution in breaking length as the result of converting strips of paper into yarn is to be noted in the case of Swedish kraft now on the market. Early published figures show quite different results to this; in fact, they show *increase* in strength as the result of conversion of paper into yarn. In spite,

however, of the diminution of strength as the result of the process according to modern practice the yarns and fabrics are much stronger now than they were some years ago.

Further tests were made on Hedychium paper stock which had been treated in a somewhat different manner, the object being to ascertain what kind of result would be obtained by twisting wet couched stuff without previous drying. The wet stuff and that made before couching was cut into ribbons by means of a water jet just before couching. After couching it contained about 43 per cent water, twisted and dried, and the breaking strain, both wet and dry, performed on each lot. The results of this are given in Table IV. In order to find out what effect the time of beating would have the yarn was made up from beaten three, three and a-half, and four hours. At three hours some of the stuff was made into paper by drying in the ordinary way, and tested for the qualities of the paper produced. The paper gave a dry breaking length of 6·8 kilometres, and had a substance of 45 grms. per square metre. It is quite evident that this stuff was not beaten in the best way to suit the paper yarn production. A point of interest here is that by cutting with water jet, couching, and twisting wet (*i.e.*, without previous drying over the drying cylinders), produces a yarn after three hours beating which is very much weaker than yarns produced from paper made in the ordinary way and then slit and twisted, but as the beating is prolonged from three to four hours the breaking length increases, and might have still further increased with further beating. The wet breaking length of the yarn so produced remained almost constant with but slight reduction up to four hours, but, relative to the dry strength, the wet strength is much diminished as the beating is prolonged. Thus, at three hours the reduction in strength as the result of wetting is 44 per cent, at three and a-half hours 55 per cent, at four hours 62 per cent.

As the paper passed over drying cylinders had a dry strength of 6·8 kilometres, but when converted into yarn (at three hours) 3·66, the actual diminution in dry strength from paper to yarn is greater when the water jet is used and no drying cylinders than when finished paper is converted into yarn as it is by modern practice. This is extremely fortunate because modern practice is a great simplification over many of the early attempts. No doubt a great deal as regards qualities of finished yarns depends upon what would appear to be small details, such as the amount of tension on the thread at the moment of re-moistening, twisting, and subsequent drying. Such details are of vital importance in the production of cellulose monofils, &c.

There is also the question of substance of paper (*i.e.*, number of grms. per square metre) coupled with width of strip which require further and systematic study. Of course the count of a yarn can be increased by increasing either the substance of the paper or its width, or both. We have already found that the best strength is got from a beaten pulp at some given substance; the general idea now is to employ a paper of from 40 to 44 grms. per square metre, and to vary its width in order to obtain the necessary weight in the yarn. Of course we also have to take into consideration the amount of twist as affecting the weight of the yarn. The great factor, however, in our opinion which has accounted for so much improvement in the quality of the yarn is the improvement in the strength and other physical qualities of the paper which is now procurable for the purpose. The early paper was more bulky and open; consequently it possessed poor strength, but was somewhat improved as the result of its conversion into yarn. The present paper is of the quality known as kraft, a thin strong rattley paper which loses some of this strength by conversion into yarn. But the initial strength of the paper is now so great and the handling qualities of same so excellent as to not only result in the production of much better yarns (in spite of some diminution in strength as the result of the process), but by reason of the use of this class of paper the output of the machines can be much increased by faster running, and the whole process of paper yarn production greatly simplified.

CHEMICAL REACTIONS AT VERY LOW PRESSURES.*

I.—The Clean-up of Oxygen in a Tungsten Lamp.

By IRVING LANGMUIR.

Continued from p. 235.

4. *Effect of Temperature of the Bulb.*—The conditions which prevail during the reaction of the oxygen with the tungsten in the present experiments differ in several essential features from those which obtain in ordinary reactions between solids and gases at atmospheric pressure.

The pressures we deal with are so low that the normal free path of the molecules is between about 1 and 10 cm. This means that relatively few of the oxygen molecules which travel from the surface of the bulb to the filament strike other molecules on the way. With the relatively small surface of the filament as compared with that of the bulb, the chance that a molecule leaving the filament should get back to the filament without first striking the bulb several times is negligibly small. The average velocity of the oxygen molecules striking the filament is therefore not perceptibly influenced by the temperature to which the filament may be heated. In other words, the filament may be at one temperature and the oxygen with which it comes into actual contact may be at a totally different temperature. At ordinary pressures this would be quite impossible, for the gas, within a layer many hundreds of times thicker than the length of the free path, would be heated nearly to the temperature of the filament, so that the gas in actual contact with the metal would be practically at the same temperature as the metal itself. That there is no great temperature drop at the surface between a metal and a gas at ordinary pressures has been amply proven (see Knudson, *Ann. Phys.*, 1911, xxxiv., 593).

A direct experimental indication that the behaviour of a gas at low pressures may be quite different from that at high pressures is easily obtained. For example, we find that with nitrogen at atmospheric pressures or even down as low as 100 microns, there is a sudden and marked increase in pressure upon lighting the filament. When, however, the pressure is 10 microns or less, there is no indication whatever on the McLeod gauge of any such change in pressure upon lighting the filament, although the sensitiveness of the gauge would be ample to detect such a change if it were relatively nearly as great as at higher pressures.

All of our previous knowledge of reactions between solids and gases is based upon results obtained when the two are at the same temperature. There were therefore no data which would indicate whether it was the temperature of the metal or that of the gas which would be the more important factor in the reaction.

In the earlier experiments (Exp. 211) the rate of clean-up had appeared nearly independent of the temperature of the filament. At that time the effect of heating the bulb to 360° and of cooling it to $-183°$ by immersing it in liquid air was tried, and it was found that the temperature of the bulb was entirely without effect. The value of ϵ obtained in these experiments was 0·0072 at a temperature of 1770° K with a filament having a surface of 0·126 sq. cm. When we found that these results were too low because of the resistance to diffusion in the tubing, it became necessary to test out the effect of the bulb temperature again with the new apparatus (Exp. 265). The bulb, however, in this case was so large that it was impracticable to cool it with liquid air, and we had to remain content with heating it to 300°. The results obtained in this way are given in Table II., Columns 3 and 5.

* Paper read before the New York Section of the American Chemical Society. From the *Journal of the American Chemical Society*, xxxv., No. 2.

It will be seen that raising the temperature of the oxygen around the filament from 25 to 300° makes no appreciable change in the value of ϵ.

This result is rather surprising. According to the ordinary conceptions of the mechanism of a chemical reaction, the effect of increasing temperature is somewhat as follows:—In order that a collision between two molecules may result in a chemical combination, the impact of the two molecules against each other must exceed a certain amount. At low temperatures no molecules, or only few, have velocities sufficient to produce strong enough impact. As the temperature rises the relative proportion of molecules which meet this requirement increases extremely rapidly, although still only a small proportion of the total number of collisions result in chemical action.

If the above theory is correct, one would expect that both the temperature of the oxygen and that of the tungsten would influence the rate of reaction. That the actual impact between such molecules would be very greatly affected by the temperature of the oxygen appears from the following considerations:—

Let us consider two molecules, one of molecular weight M_1 and the other of the weight M_2. Let v_1 and v_2 be the velocities of these molecules, and T_1 and T_2 the temperatures corresponding to these velocities. Let us

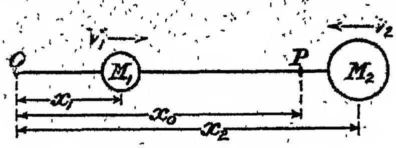


FIG. 3.

imagine these two molecules in the positions indicated in Fig. 3 moving towards each other with the velocities v_1 and v_2. Let x_0 be the distance from O to P, the centre of gravity of the system of the two molecules. Let v_0 be the velocity with which P moves from O.

By the definition of centre of gravity, we have—

$$\frac{x_0 - x_1}{x_2 - x_0} = \frac{M_2}{M_1},$$

or—

$$\frac{x_0 - x_1}{x_2 - x_1} = \frac{M_2}{M_1 + M_2},$$

and for the corresponding velocities,—

$$\frac{v_0 - v_1}{-v_2 - v_1} = \frac{v_1 - v_0}{v_1 - v_2} = \frac{M_2}{M_1 + M_2}. \quad . \quad . \quad (13).$$

Now, the impact with which they strike is proportional to the product of the mass of one of them by the velocity with which it approaches the common centre of gravity. That is, the impact is measured by $(v_1 - v_0)M_1$, but from (13) this gives for the impact I,—

$$I = \frac{M_1 M_2}{M_1 + M_2}(v_1 + v_2) \quad . \quad . \quad . \quad . \quad (14).$$

Neglecting constant factors, which would ultimately cancel out, we can place, according to the kinetic theory,—

$$T_1 = M_1 v_1^2 \text{ and } T_2 = M_2 v_2^2 \quad . \quad . \quad . \quad (15)$$

whence, combining with (14),—

$$I = \left(\sqrt{\frac{T_1}{M_1}} + \sqrt{\frac{T_2}{M_2}}\right)\frac{M_1 M_2}{M_1 + M_2} \quad . \quad (16).$$

What we now wish to find is the effect that will be produced by a change in the temperature of M_1 as compared with a change in temperature of M_2. We obtain by differentiation—

$$dI = \frac{\frac{1}{2}M_1 M_2}{M_1 + M_2}\left(\frac{dT_1}{\sqrt{M_1 T_1}} + \frac{dT_2}{\sqrt{M_2 T_2}}\right) \quad . \quad . \quad (17).$$

If we represent by dT_1 and dT_2 the temperature changes of M_1 and M_2, respectively, which will change the impact by equal amounts, we get—

$$\frac{dT_1}{dT_2} = \sqrt{\frac{M_1 T_1}{M_2 T_2}} \quad . \quad . \quad . \quad . \quad . \quad (18).$$

Taking for oxygen, $M_1 = 32$, $T_1 = 298$, and for tungsten $M_2 = 184$, $T_2 = 1600$, we get—

$$dT_1/dT_2 = 1/5 \cdot 5.$$

That is, raising the temperature of the oxygen 1° would increase the impact between the molecules as much as raising the temperature of the tungsten 5·5. From Table IV. we see that at 1600° the value of ϵ doubles in about 140° rise in temperature. Dividing this by 5·5, we see that raising the bulb temperature about 25° should double the value of ϵ if the rate of reaction is determined by the impact of the molecules. From Equation (16) it can be readily calculated that with the filament at 1600° the impact between oxygen molecules and tungsten atoms would be increased in the ratio 6·00 : 7·20 by raising the temperature of the oxygen from 25° to 300°. If the oxygen be maintained at 25° we find that to produce the same increase (*i.e.*, from 6·00 to 7·20) in impact by raising the temperature of the filament, it would be necessary to raise it from 1600° to 3160°. According to Table IV. we see that this would increase ϵ from 0·010 to about 0·200. Actually, however, we find no appreciable change in ϵ upon heating the bulb, and we must therefore conclude that it is *not* the impact of the oxygen molecules with the tungsten atoms which determines the rate of reaction.

According to the electron theory of metallic conduction of heat and electricity, metals contain free electrons which participate in the heat vibration, and have the same kinetic energy at a given temperature as the atoms of the metal. Oxygen, being an electro-negative element, easily takes up electrons, so it seems probable that an oxygen molecule would be more apt to take up an electron in striking the filament than it would to combine directly with the tungsten.

Let us consider this case from the view-point of the foregoing theory. That is, let us consider the impact of an oxygen molecule and a negative electron. We will place, therefore, in Equation (18)—

$M_1 = 32$	$T_1 = 298$
$M_2 = 0 \cdot 0005$	$T_2 = 1600$

Here, in place of $M_2 = 184$, we take $M_2 = 0 \cdot 0005$, the "atomic weight" of an electron. Whence, from (18)

$$dT_1/dT_2 = 109.$$

This completely reverses the previous result, and we see that a change of 109° in the temperature of the oxygen would have no more effect on the amount of impact between the oxygen and the electrons than a change of only 1° in the temperature of the filament. In other words, if the first step in the reaction consists of a collision between an electron and an oxygen molecule, we would expect to find just what the present experiments have shown, namely, that the value of ϵ is not affected appreciably by changing the temperature of the bulb.

This hypothesis is an entirely reasonable one. We do not need to assume that the oxygen molecule takes up more than one electron to begin with, or that the oxygen molecule is dissociated or undergoes any other change. The taking up of a single negative charge would bring into play electrostatic forces tending to hold the molecule on the surface long enough for secondary reactions to occur. These may be, for example, the taking up of more electrons, the dissociation of the molecule into charged atoms, and the combination of these with each other and with tungsten atoms to form WO_3. All these secondary reactions, however, would not influence the velocity of the reaction, since once an oxygen molecule was retained on the surface by taking up a single electron, there would then be ample time available for the subsequent changes.

On this hypothesis, the temperature coefficient of the reaction velocity may be due to two causes. First, the

increased velocity of the electrons at higher temperatures, which gives a higher percentage of them capable of giving sufficient impact to produce the reaction. Second, an increase in the number of free electrons at high temperatures might cause an increase in the reaction velocity with increasing temperature of the filament.

The electron theory seems to make it probable that the number of free electrons in a metal is very large, and that the number of them changes very little with increasing temperature (see Richardson, *Trans. Am. Electrochem.*, 1912, xxi., 69). Partly from this reason and partly because of the very high velocities of the electrons, it is probable that every oxygen molecule that strikes the filament is struck by many electrons, but is only capable of combining with those that happen to have an unusually high velocity.

There are other hypotheses, however, which may be advanced to explain the fact that ε is independent of the bulb temperature. We may assume, for example, that the surface of the metal is more or less completely covered with a film of oxide, through which the oxygen must diffuse before it can react with the metal. As the temperature of the metal increases, the oxide film would rapidly become thinner, and this fact would account for the increase in the rate of reaction as the temperature increases.

On this hyphtoesis, the oxygen would only react with the tungsten after it had diffused through the oxide film, and hence reached the same temperature as the metal. The temperature of the bulb in this case would naturally be without effect. Undoubtedly this sort of film plays an important part in gas reactions between solids and gases at atmospheric pressure (see, for example, Bodenstein and Fink, *Zeit. Phys. Chem.*, 1907, lx., 46), but it seems extremely improbable that such would be the case at very low pressures and at high temperatures. The strongest argument, however, against this theory is that the thickness of the film and hence the value of ε would vary with the pressure of the oxygen. This is, however, contrary to the results of the experiments. Another fact that indicates at least that any such film must be extremely thin is that the emissivity of the filament for both light and heat is entirely unaffected by the presence of oxygen (except below 1300°).

It must be pointed out that the reaction between oxygen and tungsten at low pressures obeys very simple laws, and does not appear to be sensitive to slight variations in the conditions. Reactions in heterogeneous systems at atmospheric pressure are usually enormously sensitive to catalytic disturbances and other irregularities which are probably characteristic of reactions that take place through an adsorbed film. Bodenstein's work on the reaction $2H_2+O_2=2H_2O$ in contact with solid bodies is an example of this type of reaction. Another example is the contact process for SO_3 (see Bodenstein and Fink, *Zeit. Phys. Chem.*, 1907, lx., 1).

For all these reasons it would seem extremely improbable that there is any surface film which limits the rate of reaction. The theory that the oxygen reacts primarily with electrons in the metal is therefore made still more probable. It will be worth while to analyse the consequences of this theory more fully.

(To be continued).

Chloral-*p*-aminoazobenzene. — Mario Mayer. — Chloral-*p*-aminoazobenzene when prepared from chloral hydrate and *p*-aminoazobenzene is a dark red powder which dissolves in a mixture of benzene and petroleum ether (in the proportions 1 : 2). From the mixed solvents two different forms of the substance can be separated, one yellow fusing at 116°, and the other red fusing at 136°. The yellow form is converted into the red form at 120°. Chemically the two forms are identical.—*Atti della Reale Accademia dei Lincei*, xxiii. [i.], No. 5.

THE SCIENTIFIC WEEK.

(From Our Own Paris Correspondent).

Possible Cause of the Migration of Salmon.

One of the most important problems of oceanography and biology is that of migrative fish. What cause guides them in their displacements and draws those that accomplish considerable voyages as do salmon? These fish often go up to rivers, and indeed go sometimes very far to milt. For this they leave the depths of the sea where they have grown up. We may then wonder what it is that incites them at the period of their reproduction to undertake a perilous peregrination. It has been said that they were carried away by the need of procuring for their eggs and for their future young fry, circumstances which alone allow of their development. But this finalist explication is open to much criticism. We must try and discover if this migrative phenomenon has no immediate determinism. M. Louis Roule, Professor at the Natural History Museum, has on this subject undertaken a series of studies, and in a paper presented before the Academy of Sciences by M. Edmond Perier, he exposes the first results at which he has arrived. He has effected his researches on the rivers of the Southern Brittany coast, and he has found that the proportion of oxygen dissolved in the water plays a very important *rôle*. According as this proportion is stronger or weaker the salmon go up the river or abstain from doing so. Salmon, doubtless like trout and other similar fish, have very intense respiratory needs, which are exaggerated at the period of reproduction. Consequently they only enter the rivers capable of satisfying these needs, thanks to the considerable amount of oxygen that their water holds in solution. Besides its scientific importance this conclusion presents an undeniable economical importance, for it will enable us to establish, thanks to a previous analysis, the list of river basins where trials of restocking will have some chance of success. It will no longer be sufficient to remove the young fry nor to construct costly ladders or scales, but one must know exactly the rivers where these works will be useful and those where they would have no effect.

New Artificial Manure.

For a long time it has been known that the nitrogen necessary to plants cannot be taken by them directly from the air. In 1886, on the roots of certain vegetable plants there was remarked the existence of large colonies of bacteria having the property of fixing the atmospheric nitrogen for the advantage of the plant on which they lived. So, then, we were in the presence of a kind of symbiosis. Great hopes were founded on these bacteria, for it was thought that the sowing of the land with these microbian cultures would considerably increase their cultural force. These hopes fell through, as did also those founded in 1901 on the azotobacter, the most powerful of the agents of nitration. The question, however, has not been abandoned, and it would seem that a solution has been arrived at. It has been found, indeed, that turf treated in a special manner constitutes a particularly favourable environment for the growth of the azotobacter, and that the grounds manured with this turf show a very notable increase in their fertility. Before inoculating the turf with the microbe, it is necessary to transform it by the action of another microbe, so as to neutralise the humic acid it contains. The technic of the operation is then the following:—The raw turf, sown with the special microbe is kept during eight or ten days at a constant temperature, then sterilised by steam. It is then inoculated with a mixture of azotobacter and nitric bacilli. After a few days' incubation at a temperature of 26° it is ready to be employed. An interesting point to be noticed is that the azotobacter continues to develop in the soil, fixing new quantities of nitrogen. The results of the experiments of

culture are most encouraging. For the culture of potatoes, whilst farm-manure increases about 40 per cent the return per acre and artificial manures about 75 per cent, inoculated turf procures an increase in the return of 123 per cent. For carrots numerous correspondents are respectively 20, 28, and 260 per cent, for turnips 26, 47, and 100 per cent. If these results are confirmed by other experiments, and if this new produce for manuring suits all grounds, the manures of electricity will have a most serious rival to face, with whom they will have to undertake a very severe struggle.

SILICA FORMS THE HALF OF THE EARTH'S CRUST.

The terrestrial crust is formed especially of silica, and this fact is generally little known. It is because silicium and its derivatives are, for a reason unknown, the poor children of chemistry and mineralogy. In the treatises on chemistry employed in secondary education a small place is given to silica and to silicium, but the silicates are completely ignored. Prof. Henry Le Chatelier, Professor at the Sorbonne and Member of the Academy of Sciences, only explains this abstention of chemists by the somewhat routine respect of a too distant tradition. He has just put an end to these errors by giving to silica and to silicates the place that is their due. Silica is the most abundant of the chemical combinations existing in the crust of the earth. People have tried to form an idea of the average composition of the solid crust of our globe by making in different countries analyses of a very great number of rocks. Several thousands of samples have been taken, especially in the United States and in Norway. The results have been almost identical, and the corresponding figures may be corresponding figures may be considered as giving a pretty exact average for the whole world. The terrestrial crust thus contains 58·2 per cent of silica, 15·8 per cent of alumina, 7·1 per cent of oxides of iron, then some oxides of sodium, of potassium, of calcium, of magnesia, in proportions varying from 3·2 to 5·2 per cent. The crust of our globe contains also 1·5 per cent of water and 1 per cent of oxide of titanium. This silica is found partly in a state of free silica, often in a state of combined silica. The silicates are very numerous; felspars, micas, pyroxenes form the principal families. Among the hydrated silicates we must mention, in the first place, clay, then compound silicate of iron, of magnesia, and of potash, constituting the green sand by which the artesian waters of Champagne and Normandy arrive in Paris. As to the industrial importance of silica it is immense. The silicated rocks, granites, porphyries, schists, &c., are employed as materials for building. The Vosges stones, which were used to build the Cathedral of Strasbourg, the mill-stone, a variety of chalcedony that is exploited in the neighbourhood of Paris, are likewise only silicates. The mill-stone, unalterable by the atmospheric agents and possessing the property of making one body with the cement, allows of the erection of buildings which are, so to say, indestructible. So it is employed systematically for the walls of prisons. Lastly, the ceramic industry, as well as the glass industry, are entirely based on the utilisation of siliceous matters. Glass, which is considered unalterable, is, on the contrary, very sensitive to the action of the temperature and of liquids. M. Henry Le Chatelier has particularly studied this important question of the chemical alterability of glass. The alteration of different glasses can sometimes be remarked without the employment of any precise measurement. Antique glass found in the soil shows an iridescent layer, superficial and deprived of transparency on account of the elimination of a part of the elements constituting the glass. This iridisation, which is so pretty, can, it is true, be produced artificially by heating during a few hours ordinary glass vases in chlorhydric acid diluted. Spherical bulbs thus treated have exactly the appearance of soap-bubbles. In other parts of the work Prof. Henry Le Chatelier studies the physical and optical properties of glass, metallic alkaline silicates, magnesias, and ceramic.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, May 7, 1914.

Sir WILLIAM CROOKES, O.M., President, in the Chair.

PAPERS were read as follows:—

"*Some Calculations in Illustration of Fourier's Theorem.*" By LORD RAYLEIGH, O.M., F.R.S.

"*Theory of Long Waves and Bores.*" By Lord RAYLEIGH, O.M., F.R.S.

"*Protection from Lightning and the Range of Protection Afforded by Lightning Rods.*" By Sir JOSEPH LARMOR, F.R.S., and J. S. B. LARMOR, M.A.

On modern ionic views discharge in the atmosphere should originate at a place of maximum intensity of electric field and spread both ways from it along a line which should be roughly the line of force. The explanation of branching, zigzag, and multiple lightning discharges is to be sought on these lines. The introduction of a narrow linear conductor cannot sensibly disturb a steady field of force, and not at all if it is transverse to the field. Thus it would seem to be the top of the building itself, not of the lightning conductor, that attracts the discharge, and the function of a single rod can only be to lead it more safely away. But a number of rods distributed over the area of the roof, and effectively connected to earth by a conductor, can, by their joint action, lift the intensest part of the field from the top of the building to the region around their summits, and so obviate or much mitigate the danger of discharge from above to the building which they cover. In illustration, diagrams are given of a vertical field of force as disturbed by vertical pillars of semi-ellipsoidal form and of various breadths, or by an earthed conducting region overhead such as might be originated by gradual discharge from a pointed rod.

"*Newcomb's Method of Investigating Periodicities and its Application to Brückner's Weather Cycle.*" By Prof. A. SCHUSTER, Sec. R.S.

"*Flow in Metals Subjected to Large Constant Stresses.*" By E. N. DA C. ANDRADE.

The law connecting the extension with time for wires of various metals subjected to large stresses has been examined at different temperatures. The stress was kept constant throughout the flow by the device of a hyperbolic weight employed in former experiments. The different types of flow observed for different metals at room temperature are only particular cases of one general law governing the flow of all single metals, and can all be found for one metal by choosing an appropriate temperature; thus, soft iron at 450° C. behaves similary to lead at 15° C. The formula $l = l_0(1+\beta t^{1/3})e^{\kappa t}$ can be made to represent the increase of length l with time t in all cases by suitable choice of the constants l_0, β, κ. The viscous part of the flow, expressed by κ, does not exist at low temperatures, but becomes more and more predominant with rise of temperature. The distinction of the viscous part of the flow from the initial part of the flow, and the behaviour in general, can be explained from the co-existence of the crystalline and the amorphous state in the metal.

The behaviour of wires of solid distilled mercury shows that the rapid initial flow characteristic of the single metals is not due to impurities.

Duplex alloys behave altogether differently to the single metals with respect to the flow, the anomalous behaviour corresponding to a difference in type of crystalline structure.

"*Eddy Motion in the Atmosphere.*" By G. I. TAYLOR.

The paper contains a theoretical discussion of the function of eddies in conveying heat and momentum through a fluid. It is shown also that measurements of the temperature of the air over the Great Bank of Newfoundland made

by the author last year, lead to the conclusion that eddies extend upwards over the sea to a height of at least 800 metres; and that there is no appreciable diminution in their size or intensity in this height.

On the assumption of a uniform amount of eddy motion, the velocity of the wind at various heights above the ground is calculated, and shown to agree with the most recent observations carried out over Salisbury Plain. The actual amount of eddy motion is calculated both from wind velocity and from temperature measurements, and the two values are found to agree within the limits of error. This tends to confirm a general theorem about eddy motion in two dimensions which is deduced from theoretical considerations.

"*Properties of Magnetically-shielded Iron as Affected by Temperature.*" By Prof. Ernest Wilson.

In a paper recently read before the Royal Society, it is shown that if stalloy in ring form is shielded from the earth's magnetism and subjected to a considerable magnetising force at atmospheric temperature, the permeability can be increased. The present experiments deal with the effect of allowing stalloy to cool down through the temperature at which it regains magnetic quality when in a shield and when under the influence of a magnetising force due to a continuous current. Two specimens have been subjected to this treatment, and in each case the maximum permeability has a value of over 10,000 when the specimen is at atmospheric temperature. The dissipation of energy by magnetic hysteresis for a given value of the magnetic induction is reduced by the treatment.

ROYAL SOCIETY CONVERSAZIONE.

The Royal Society Conversazione, held on Wednesday, May 13th, at the Rooms in Burlington House, was quite up to its usual level of interest.

Short demonstrations were given during the evening by Prof. J. P. Hill, F.R.S., on the Percy Sladen Expedition to Brazil, 1913, illustrated by numerous lantern slides and views of the regions visited. Also by Mons. P. Schilowsky, upon The Application of Gyroscopes to the Three Systems of Locomotion; on land, on sea, and in the air. Gyroscopes with models of monorail cars, ships, and aeroplanes were used to illustrate the lecture.

Among the more striking exhibits were the following:—

Mr. C. R. Darling. Some New Surface Tension Phenomena, and an Experiment to Show the Structure of Liquid Jets.

A globule of oil was formed on the surface of water, and a drop of quinoline allowed to fall upon it. On this drop reaching the oil-water interface, the globule burst with considerable violence. Orthotoluidine globules were formed on a water surface, and a large globule of dimethyl-aniline was added, which then proceeded to absorb the orthotoluidine. The process of absorption resembled the feeding of certain lower organisms. The experiments were made visible to the audience by projection upon a screen and the extraordinary motions due chiefly to surface tension were watched with considerable interest.

Prof. Leonard Hill, F.R.S., and Mr. O. W. Griffith. The Caleometer.

The caleometer is an instrument designed to measure the degree of comfort in a room, or a public hall, or a factory, in so far as that depends on the rate of cooling of the human body. Comfortable conditions are indicated by gentle oscillations of the pointer—about a mean value of 30 calories per minute. A low steady reading denotes monotony and oppressiveness; violent oscillations about a high mean value are evidence of excessive cooling by an unpleasant draught.

Mr. W. A. Douglas Rudge. Electrification produced during the Raising of a Cloud of Dust.

A delicate electroscope was attached to a metallic rod tipped with radium, which ionised the air in the neighbourhood. The electrification caused by blowing dust out of a bottle was indicated by the charging of the electroscope. Dust of an acidic nature, silica, or molybdic acid gave a negative charge, while metallic oxides and organic bases gave a positive charge.

Mr. C. V. Boys, F.R.S. Blower for very Large Soap Bubbles.

The difficulties of blowing and detaching very large soap bubbles were overcome by a special form of injector blowpipe swivelled at right angles to its length about the injector nozzle as an axis, and with a diverging cone of flexible fabric with a serrated edge, made impervious to liquid a short distance behind the serrations. This cone was kept open by two springs. The absorbent material, up to the impervious band, provided liquid sufficient for a large thin bubble, but not so much as to make it unduly thick, for the limit of possible diameter of a bubble is greater as its thickness is less, and the points of the serrations feed the bubble in numerous very fine streams. Bubbles 3 or 4 feet in diameter are possible, and by injecting a little warm air during their formation they can be made to rise and they then form magnificent objects.

Mr. Louis Brennan, C.B. The Iridoscope.

A device by which it is possible to make a large sheet of soap film. By standing the frame holding this film upright in a suitable light fine displays of colour are produced by the natural thinning of the upper portion of the film, or by playing upon it by a jet of air.

Mr. W. Duddell, F.R.S. Water Model of the Electric Arc.

The model exhibited consisted of a mushroom valve. The pressure tending to reseat the valve was so arranged that it diminished very rapidly as the valve lifted. In this way, when the flow of water was increased through the valve, the difference of pressure between its two sides decreased and thus represented one of the properties of the electric arc. When a steady flow was established and a column of water having a definite periodic time connected to the valve oscillations were set up similar to those obtained with an electric arc.

The Silica Syndicate, Ltd. Some New Developments in the Manufacture of Apparatus in Transparent Quartz Glass.

The Silica Syndicate had a large number of exhibits. A great advance has recently been made by the invention of a method of making an air-tight seal between quartz glass and metal, which consists essentially in flowing pure lead into the hot quartz tube in a vacuum; the metal makes perfect contact with the quartz, and vacuum apparatus of all descriptions can be constructed in this way. Electric lamps, X ray tubes, electric radiators, and other apparatus to which the lead seal was successfully applied were shown.

The Polychromide Company (The Dover Street Studios, Ltd.). Instantaneous Photographs on Paper Taken in Natural Colour by the Polychromide System.

The optical separation of the natural colour of the object photographed is accomplished by means of the Hamburger-Conrady colour separation camera, which exposes three plates simultaneously—representing the red, yellow, and blue sensations in the superposed positives on gelatino-silver emulsions, which constitute the complete colour records exhibited. A very fine collection of photographs were shown, including one of the President of the Society; the colour rendering was excellent, and the exhibit caused great interest.

The British Museum (Natural History). A Selection of the Specimens Collected on the British Antarctic ("Terra Nova") Expedition, 1910—1913, under the Leadership of the late Capt. R. F. Scott, C.V.O., R.N.

Mr. F. W. Aston. A Simple Microbalance for the Determination of the Densities of Small Quantities of Gases.

The balance was made entirely of fused quartz, and consisted of a beam of the simplest possible construction, bearing at one end a small closed bulb and at the other a solid counterpoise. The whole was supported by a knife edge working on a polished quartz plate, and enclosed in a small case made of plates of glass in such a way that the pressure could be varied at will. The capacity of the whole "case" was about 2 cc., and the movement of the balance could be watched through a small telescope. It was sensitive to about one-millionth of a mgrm.

Mr. Rollo Appleyard: Chain Apparatus for the Approximate Measurement of Logarithmic and Hyperbolic Functions.

The apparatus consists of a chain suspended so as to form one half of a true catenary, and it is shown that by suitably proportioning the scale of measurement to the tensions of the chain the various quantities required can be obtained, to a first degree of approximation, by direct measurement from the suspended chain. These quantities include (1) the base of the Napierian logarithms; (2) the anti-logarithms of numbers to the Napierian base; (3) the hyperbolic function, Sin x, Cos x, Tan x, and Sec x. Special interest attaches to the apparatus, as it is just 300 years since the invention of logarithms by Baron John Napier, of Merchiston.

Prof. A. W. Bickerton. The Polyscope.

A kaleidoscope rendered so optically perfect that a hundred reflections of a point or object may be seen. The angles of one are 30°, 60°, and 90°. Of the other, two angles 45° and one of 90°. They produce two classes of patterns, one suitable for textile fabrics, cretonnes, &c., the other suitable for floor cloths, tiles, &c.

Messrs. Chance Brothers and Co., Ltd., showed a number of specimens of Glass for Making Spectacle Lenses for the Absorption of Ultra-violet and Infra-red Rays and for the Reduction of Glare, based on experimental results given in Sir William Crookes's recent paper read before the Royal Society. Some of these glasses have the valuable property of almost completely absorbing the heat and ultra-violet radiations, and are useful for many purposes besides spectacles.

Exhibits were also given by the Marine Biological Association, Profs. MacBride, A. F. Stanley Kent, E. B. Paulton, the Astronomer Royal, and many others.

PHYSICAL SOCIETY.

Ordinary Meeting, May 8, 1914.

Dr. A. Russell, Vice-President, in the Chair.

A paper entitled "*Some Gyrostatic Devices for the Control of Moving Bodies*" was read by Dr. J. G. Gray.

The paper dealt with a number of new contrivances for stabilising, steering, and forcibly manœuvring moving bodies, such as torpedoes and airships.

A number of old experiments were first shown. These included the "gyrostat on stilts" and "gyrostat on gimbals" experiments due to Lord Kelvin, the "crossed bifilar" experiment due to Prof. Blackburn, and a stilt top devised by Prof. Harold Wilson. It was shown that the gyrostatic system in each of these experiments, although exhibiting considerable balancing power, was not possessed of real stability. An unstable body rendered truly stable by gyrostatic action must possess the property that if displaced from the mean position it returns to, and comes to rest in, that position. The mean position is that in which the potential energy of the gyrostatic system is a maximum, and if the system is disturbed energy must be supplied to restore it to the mean, or undisturbed, position.

A number of new gyrostatic models were displayed in action. These include two-wheeled and four-wheeled gyrostatic motor cars and bicycles. These all provide examples of gyrostatic systems provided with complete or real stability, and in all the cases shown the stabilising forces are derived from the propelling system.

One of the cars shown runs on two wheels in tandem, and is stabilised by a single gyrostat. This gyrostat is mounted in the car and controls the steering mechanism; it forms, in fact, a gyrostatic chauffeur. The model illustrated a new form of torpedo and airship control.

A second form of motor car, which also runs on two wheels in tandem, consists of two parts, a front one and an after one. The front part carries a gyrostat, the back part the propelling mechanism, and the two parts are connected together by means of a vertical hinge. The front part is propelled by the back part, and the arrangement is one of complete stability. The entire system may be manœuvred by means of the gyrostat. It was pointed out that by properly fitting an airship with a gyrostatic "nose" it should be possible to manœuvre forcibly the airship by means of forces derived from the propellers.

The bicycles, which are provided with gyrostatic riders, are examples of moving bodies steered by gyrostatic action. The action is quite different from that of an ordinary bicycle. They are not "momentum" instruments.

The devices shown are at once applicable to long-distance torpedoes, both submarine and aerial. The gyrostatic system may be operated by the wireless transmission of electrical action.

At the conclusion of the paper the author showed a new series of animated gyrostats.

Discussion.

Dr. W. Watson thought the mechanisms shown were of great theoretical importance. He gathered, however, that the author himself thought they were more of theoretical than practical interest. He concluded some time ago that a two-wheeled car would not be of much use, as, although gyrostatic control worked satisfactorily either on a straight path or on a curved path of constant curvature, any attempt to alter the curvature had to be made with great caution. Hence a train built on this system would have to slow up on approaching either the beginning or the end of a bend. With a motor car, where one had to steer immediate courses on account of other traffic, the arrangement would be impracticable. At one time, when some cars had engines laid longitudinally and others transversely, makers of the latter type claimed that gyrostatic action came into play and tended to prevent skidding. However, unless the gyrostat was free to move relatively to the car, one might as well have a lump of iron in its stead. He had investigated the amount of relative motion which might take place due to give in the springs or mountings, and it was quite insufficient to allow of appreciable gyrostatic action.

Mr. Duddell complimented the author on the collection of beautiful models which he had brought before the Society and the admirable way in which he had explained the principles underlying their action. He asked what speed was attained by the flywheels of the gyrostats.

Mr. R. S. Whipple also expressed his admiration of the models.

Mr. F. J. Whipple asked if the author had worked out the theory of the ordinary bicycle, and if it was his considered opinion that the rider had to perform the actions which he had described in steering. It was his opinion that when travelling rapidly this was not so, and that there was a stabilising effect due to the gryrostatic action of the front wheel. This was particularly noticeable in the way in which the wheel seemed to be pulled back into position if, when riding without the hands, the cyclist encountered a small stone.

Dr. Russell asked concerning the use of the word "gyrostat." He remembered on one occasion when Lord Kelvin was showing some of these experiments to von Helmholtz an accident occurred which resulted in one of the gyroscope wheels passing through Helmholtz's silk hat. After that it was customary to enclose the gyroscope

in a brass case, and it was then usually called a gyrostat. He did not quite see why.

The Author, in reply, said that the larger gyrostats could be taken up to a speed of 20,000 revs. per min. in half-a-minute, and would run for 75 minutes. In steering a bicycle the rider turns the front wheel to the side to which the machine leans, and the forward momentum brings it up to the vertical position. The gyrostatic action helps, but only to a very slight extent. The name "gyro stat" was the one invariably used at Glasgow since Lord Kelvin's time.

A paper entitled "*A Graphic Treatment of Cusped Wave-fronts, and of the Rainbow*," by Mr. W. R. Bower, was taken as read in the absence of the author.

A method of drawing the cusped wave-fronts produced by refraction and reflection at a spherical surface and a graphic treatment of the elementary theory of the rainbow are described in the paper. The method is based upon the properties of the centre of juuction. In the case of reflection at a spherical surface in which aplanatic points are not available the position of the junction centre is obtained by elementary geometry.

By the use of junction-centres the distribution of the successive foci obtained on refraction and reflection at a spherical surface is readily plotted. If in the case of a rainbow it is assumed that the emergent portion of the effective pencil, as well as the incident portion, is one of parallel rays, then the distribution of foci with regard to the drop is a symmetrical one.

The caustics on refraction and reflection are also readily drawn as loci of points and envelopes of rays. Hence the wave-surfaces can be obtained. These in some regions are cusped, and the caustics are the loci of the cusps.

In the case of pencils that are effective in producing rainbows, the lengths of the incident portion of the chief ray intercepted by the spherical drop of radius, r, and a concentric sphere of radius, $r\mu$, are in the ratio 1 to $n+1$, where n is the number of internal reflections. This leads to a geometrical construction for finding the points of incidence of the chief rays of the effective pencils. These rays are at minimum deviation, and the same chief ray remains at minimum deviation, although the associated pencil may be converging or diverging.

SOCIETY OF CHEMICAL INDUSTRY.

(London Section).

Ordinary Meeting, May 4, 1914.

Prof. W. R. E. Hodgkinson in the Chair.

The following papers were read and discussed :—

"*A Reaction of Tetranitromethane.*" By W. R. E. Hodgkinson.

The author describes a solvent action in certain metals, *i.e.*, such as form amides or amino-like compounds, of an alcoholic ammoniacal solution of tetranitromethane. When the metal is placed in such a solution a yellow colour develops, the temperature rises, and there is a slight gas evolution $(N_2)(CO_2)$. The action only becomes vigorous with copper after a small quantity of the blue cupramine compound has formed. When a cupramine solution is added to an alcoholic solution of tetranitromethane crystals form rapidly. They are identical with those formed from the metal. Similar results were obtained with nickel, zinc, cadmium-amine solutions, and with ammonium double salts of the metals. The salts appear to be of the general type $C(NO_2)_3$, NHM'_3, NH_3. They are nearly all deliquescent, and when rapidly heated explode.

"*Application of Jets for Mixing.*" By Dr. Oscar Nagel.

The low efficiency of jets is caused by the fact that about 75 per cent of the energy is consumed in the whirl which is formed in the transit of the jet from one nozzle to another. This whirl effects the most intimate mixture of the motor-jet with the medium to be moved.

The use of jets as mixers is therefore suggested for various operations, such as the chamber process of manufacture of sulphuric acid. Preliminary experiments in this direction have been successful.

"*Apparatus for the Automatic Measuring and Injection of Chemicals.*" By the Hon. R. C. Parsons, M.A., M.Inst.C.E.

The author having referred to the crude methods gener ally adopted for introducing chemicals into water previous to its being filtered, proceeded to describe his low pressure injector, known by the name of the "Tiltometre," which is operated by means of the pressure obtained by inserting a venturi tube into the main in which the water to be treated flows. He then gave the results of the tests of this intrument, which proved to be an accurate and reliable apparatus for automatically treating water with a constant percentage of chemical, although the flow varies considerably.

He next explained his "High Pressure Chemical Injector," which also works by means of the pressure derived from a venturi tube inserted in a main.

This apparatus can inject against any pressure, and consists of two cylinders in which pistons having wide circumferential grooves move quite freely, and by means of a controlling valve are made to eject the chemical alternately, thus maintaining a regular flow. Above the cylinders are the inlet and outlet valves, the former for admitting the chemical from a tank in which it is stored, and the latter through which it is injected into the main. One one side of this instrument is a manometer for indicating the venturi pressure due to the flow through the main, and on the opposite another manometer attached to a small venturi tube through which the chemical ejected passes, and the amount discharged measured. The ratio of these discharges gives the percentage of chemical added, and can be adjusted by the regulating valve.

Both these instruments are shown to be simple, durable, reliable, and to yield very accurate results.

SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

Ordinary Meeting, May 6, 1914.

Mr. A. Chaston Chapman, President, in the Chair.

Messrs. Lauchlan Henry Dyke Acland, Walter Alan Gibbings, Frederic Herbert Lees, and William Henry Woodcock were elected Members of the Society.

Certificates were read for the first time in favour of Messrs. William Roscoe Hardwick, B.Sc., F.I.C., 13, Batavia Buildings, Hackins Hey, Liverpool ; Harold Fletcher Hills, F.C.S., Commercial Gas Works, Stepney, E. ; Robert Hindle Kay, 72, Manor Road, Stoke Newington, N.

"*Detection of Castor Seeds.*" By G. D. Lander and J. J. Geake.

A modification of the precipitin reaction as practised by Mooser and others, whereby direct extraction of a suspected material by means of physiological saline replaces the more costly and tedious method of extraction by glycerol.

"*Composition of Milk and Milk Products.*" By H. Droop Richmond.

As in previous years, the author gave a summary of the results of the analyses made in the Aylesbury Dairy Co., Ltd., during 1913 ; a sample of goat's milk and one of human milk was examined. It was shown that the aldehyde figure of cream calculated on the portion free from fat was the same as that of milk.

"*Note on 'Sharps'.*" By J. F. Liverseege and G. D. Elsdon.

The permissible percentage of calcium sulphate in "sharps" (from grain) was discussed and a series of analyses of known samples was given.

"*Action of Weak Acids on Soluble Fluorides.*" By P. A. Ellis Richards, F.I.C.

The author shows that the fluorides of the alkali metals are decomposed by many organic acids, including acetic, formic, tartaric, malic, lactic, benzoic, and salicylic acids, with liberation of hydrogen fluoride. Carbon dioxide gas passed through a solution of either sodium or potassium fluoride has a similar action.

"*Simple Form of Fat Extractor.*" By G. A. Stokes.

A simple fat extraction apparatus can be constructed by suspending a fat-free extracting thimble by means of wire in a long necked conical flask. The wire is fixed, and can be raised and lowered in the stopper, in which a condenser is fitted in the usual way.

INSTITUTE OF METALS.

May Lecture.

The annual May lecture of the Institute of Metals was delivered by Prof. E. Heyn, of Berlin, in the evening of Tuesday, May 12th, at the Institution of Chemical Engineers, Engineer Vice-Admiral Sir Henry J. Oram, K.C.B., F.R.S., President of the Institute of Metals, being in the Chair.

Prof. Heyn said that it was a well-known fact that the welfare and convenience of modern mankind was, to a very considerable extent, influenced by the achievements of the engineer. People admired his work, and were daily confiding life and health to his creations. But only few were conscious of the fact that engineering work was, to a great amount, dependent on the possibility of manufacturing sound materials fit for the purpose and of keeping them sound in the course of the manifold processes that these materials required to go through until they were assembled into the admirable engineering structures presenting themselves to the public eye. Few persons were conscious of the enormous amount of thought bestowed on the question of soundness of materials by thousands of men fighting continuous struggles against the numerous hidden dangers involved in the intricacy of structural material and working strenuously towards its perfection and reliability.

Certain structural members might fail even without being subjected to stresses in service. For instance, it had often been observed that condenser tubes made out of brass cracked simply when stored up in the yard. Some articles made out of this metal, when exposed to atmospheric in uences, underwent an alteration to such an extent that they might be crumbled between the fingers. Similar phenomena could be stated in structural members made out of other metals and alloys, when they were manufactured under unfavourable conditions, which lead to serious internal strains.

The author said that he had made a special study of the phenomena connected with internal strains, investigating their causes and devising a method for measuring their amount. In his lecture the author dealt specially with the internal strains produced by cold working of metals (cold drawing, cold rolling, cold hammering, &c.). He showed that by these operations under unfavourable conditions internal strains might be set up in structural members which came close to their resisting power, so that even trifling additional strains caused by external forces or other circumstances (scratching of the surface, unequal heating or cooling, slight corrosion by certain agents, which were contained in the atmosphere or by certain paints) might lead to unforeseen fracture. He discussed the means for removing or diminishing such dangerous internal strains, and illustrated his lecture by numerous samples taken from the domain of practical engineering.

NOTICES OF BOOKS.

The Synthetic Use of Metals in Organic Chemistry. By Arthur J. Hale, B.Sc.(Lond.), A.I.C. London: J. and A. Churchill. 1914.

For advanced students of organic chemistry this will be found a very useful handbook. The different types of reactions effected by the metals and their salts are described, with references to the original papers relating to them, and full directions are given for practical work illustrating some of the more important reactions. The student who has a fair general knowledge of the operations of practical chemistry will be quite well able to carry out the experiments without any help from a demonstrator, for the directions are very explicit, and quantities employed and yields to be expected are always stated. For the chapters on practical work, which form perhaps the most useful part of the book, the information has been collected from many foreign periodicals, and it will be a boon to students who do not read German and French easily, or to those who cannot readily get access to the *Berichte*, &c.

A Third Year Course of Organic Chemistry. By T. P. Hilditch, D.Sc.(Lond.), F.I.C. London: Methuen and Co., Ltd. 1914.

This book is the sequel to Dr. Dunstan's "First Year Organic Chemistry" and Mr. F. P. Thole's "Second Year Organic Chemistry," and deals with the heterocyclic compounds, and also with some of the more complex aliphatic and carbocyclic compounds not discussed in the earlier books. These include the sugars, polypeptides, and terpenes. The book will be found a useful and safe guide for candidates for such examinations as the Honours B.Sc. degree of London University. The author has introduced many valuable summaries and schemes showing constitutions, which are likely to impress themselves on the student's memory, and he has been judicious in selecting his material well, and not overburdening the text with details. It is a pity that small print has been used so much, for the type in which some of the formulæ are printed renders them almost undecipherable.

Karbide und Silizide. ("Carbides and Silicides"). By Prof. Dr. Otto Hönigschmid. Halle-a.-S: Wilhelm Knapp. 1914. (Mk. 13.60).

This monograph treats from a scientific point of view of the binary compounds of carbon and silicon with other elements, and gives a very complete account of the subject. Technical processes and patents are not, as a rule, included for discussion, but all laboratory work on carbides and silicides is very fully described. The early sections deal with the preparation and properties of carbides in general, and then each individual compound is described in full. The silicides are treated similarly, and the monograph concludes with an appendix contributed by Dr. Otto Flaschner on the thermic analysis of silicides and carbides.

Contribrición al Estudio de la Imagen Latente Fotografica. ("Contribution to the Study of the Photographic Latent Image"). By Luis Guglialmelli. San Martin: Imprenta de "El Nacional." 1913.

This volume contains a thesis presented to the University of Buenos Aires by the author for his doctorate. It gives a critical summary of the various hypotheses concerning the latent image which have been put forward, grouping them as physical, chemical, and physico-chemical. The last class, and in particular the colloidal theory, is considered in the greatest detail, the author believing that the bulk of the evidence that has been accumulated is in its favour.

CORRESPONDENCE.

WEBSTER FUND.

To the Editor of the Chemical News.

Sir,—Will you kindly allow me to announce through your columns that the fund subscribed in 1910 on an appeal for which I made myself responsible, and devoted to the relief of Mr. Charles S. S. Webster, of Bristol, research chemist, is now exhausted. Some £200 was raised, and paid into an account at the London County and Westminster Bank, Bayswater Branch. After providing for immediate necessities, the remainder (£150) has been paid over in monthly payments of £4. The situation of the family is still one of the greatest necessity, and if any of your readers would subscribe a further amount it will be dealt with in the same way. On a first appeal I have a promise of an annual payment of £10 over a period of three years.

Communications to the undersigned, or cheques made payable to the Manager, London County and Westminster Bank, Bayswater Branch, and crossed C. S. S. Webster Fund.—Yours, &c.,

C. F. Cross.

4, New Court, London, W.C.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xlvii., No. 5, 1914.

Active Modification of Nitrogen.—H. B. Baker and R. J. Strutt.—Tiede and Domcke have stated that the luminescence of active nitrogen is not observed if the gas is absolutely free from oxygen. The authors, however, find that this is not the case. They point out that the luminescence has never been put forward as a proof of the presence of active nitrogen, but that the ground for the conclusion that an active modification is present is the formation of hydrocyanic acid, for example, when the gas from a vacuum tube is led through organic compounds containing hydrogen. The luminescence appears in nitrogen which has been exposed to the action of phosphorus (thus removing all oxygen) for a long time, and the nitrogen evolved from potassium nitride also gives it.

Hypoborates from Gaseous Boron Hydrides and Bases.—Alfred Stock and Ernst Kuss.—B_4H_{10} and B_2H_6 give the same substance when they react with alkalis. In each case hypoborates are formed, the re. actions being $B_2H_6+2KOH = 2KOBH_3+H_2$, and $B_4H_{10}+4KOH=4KOBH_3+H_2$. $KOBH_3$ is hygroscopic, hydrogen being evolved at the temperature of the room. $KOBH_3+H_2O=KBO_2+5H$. Alcohol dissolves the hypoborate, which undergoes partial decomposition. Acids, especially acetic acid, decompose the salt or its solution simultaneously. $KOBH_3+HCl+2H_2O = H_3BO_3+KCl+5H$. With solutions of nickel salts a black insoluble nickel boride, Ni_2B, is obtained. When potassium hypoborate is heated to about 500° it loses a large part of its potassium in the metallic form.

New Type of Complex Tungsten and Molybdenum Cyanides.—Oscar Olsson.—A series of complex cyanides of tetravalent tungsten which are analogous to the molybdenum cyanides of the type $Me_4Mo(CN)_8.xH_2O$, can be obtained from $K_3W_2Cl_9$. Where these compounds are titrated with potassium permanganate they are not converted into tungstic acid but into complex pentavalent tungsten cyanides of the general type $Me_3W(CN)_8.xH_2O$. It is probable that the anomaly in the valency determination of molybdenum with permanganate in the complex cyanides of the type $Me_4Mo(CN)_8.xH_2O$ is to be ascribed to the formation of pentavalent complex molybdenum cyanides, and that the compounds $Me_4Mo(CN)_8.xH_2O$ are to be regarded as derivatives of tetravalent molybdenum.

Atti della Reale Accademia dei Lincei.
Vol. xxiii. [i.], No. 5, 1914.

Oximes of α-Naphthylphenyl Ketone.—Mario Betti and Pasquale Poccianti. — α-Naphthylphenyl ketone, $C_{10}H_7.CO.C_6H_5$, being an asymmetrical ketone should give two isomeric oximes. By the action of hydroxylamine upon α-naphthylphenyl ketone the authors have obtained a mixed product with no sharp melting-point, which when re-crystallised from alcohol gives a compound of constant melting-point and uniform aspect. If hydroxylamine liberated from its chlorhydrate by means of alkali is used, the product is chiefly the isomer which melts at 127°, but if the chlorhydrate is used with no alkali the other isomer, melting at 161°, predominates. A mixture of equal quantities of the two compounds melts at 135—140°, and a mixture of two parts of the 161° compound with one of the 127° compound melts at 140—145°, and it is possible that the mixture is the oxime (m. p. 140—142°) described by Kegel. When the 127° compound is dissolved in ordinary alcohol acidified with dilute hydrochloric acid it is transformed into the 161° compound. The same transformation also takes place spontaneously.

MISCELLANEOUS.

Association of Teachers in Technical Institutions.—The Association of Teachers in Technical Institutions will hold its Eighth Annual Conference at Liverpool during Whitsuntide, May 30 to June 3. The educational meetings will be held in the Large Hall of the Central Municipal Technical School. This Association is the only representative body of Technical Teachers in the kingdom, and its Conferences are therefore of considerable importance in the educational world. The open meetings begin on Monday, June 1, at 10.30 a.m., when the Chairman of the Liverpool Education Committee, Councillor J. W. Alsop, B.A., J.P., will welcome the Conference to Liverpool, and the President, Mr. P. Abbott, B.A., will deliver his Presidential Address. During the Conference papers will be read by Mr. W. Hewitt, B.Sc., the Director of Technical Education for Liverpool, Prof. Haldane Gee, Mr. W. E. Harrison, Mr. Laurence Small, Mr. W. R. Bower, and others. Sectional meetings will be held on the afternoon of June 2, when papers of special interest to the various sections of Technical Education will be read. Resolutions on matters of educational and professional interest will be discussed at the various meetings. The Annual Dinner will be held at the Exchange Station Hotel on the evening of June 1. Visits to Port Sunlight and Messrs. Cammell Laird and Co.'s works, and a reception by the Lord Mayor at the Town Hall, are amongst the many social items which have been arranged by the Conference Committee, and an Exhibition of Books and Scientific Apparatus will be held throughout the Conference at the Technical School. —J. Paley Yorke, Hon. Secretary, 55, Filey Avenue, Upper Clapton, N.

MEETINGS FOR THE WEEK.

Tuesday, 26th.—Royal Institution, 3. "Natural History in the Classics," by Prof. D'Arcy W. Thompson C.B.

Thursday, 28th.—Royal Institution, 3. "Identity of Laws, in General and Biological Chemistry," by Prof. Svante Arrhenius, D.Sc., &c.

— Royal Society. "Studies of the Processes Operative in Solutions—XXIX., The Disturbance of the Equilibrium in Solutions by 'Strong' and 'Weak' Interfering Agents," by H. E. Armstrong and E. E. Walker. "Type-reading Optophone," by E. E. Fournier d'Albe. "An Application of an Electrolytically-produced Luminosity forming a step towards Telectroscopy" by L. H. Walter. "Convection of Heat from Small Cylinders in a Stream of Fluid and the Determination of the Convection Constants of small Platinum Wires with applications to Hot-wire Anemometry," by L. V. King.

Friday, 29th.—Royal Institution, 9. "Plant Autographs and their Revelations," by Prof. J. C. Bose, M.A.

Saturday, 30th.—Royal Institution, 3. "Fiords and their Origin," by Prof. J. W. Gregory, F.R.S., &c

THE CHEMICAL NEWS

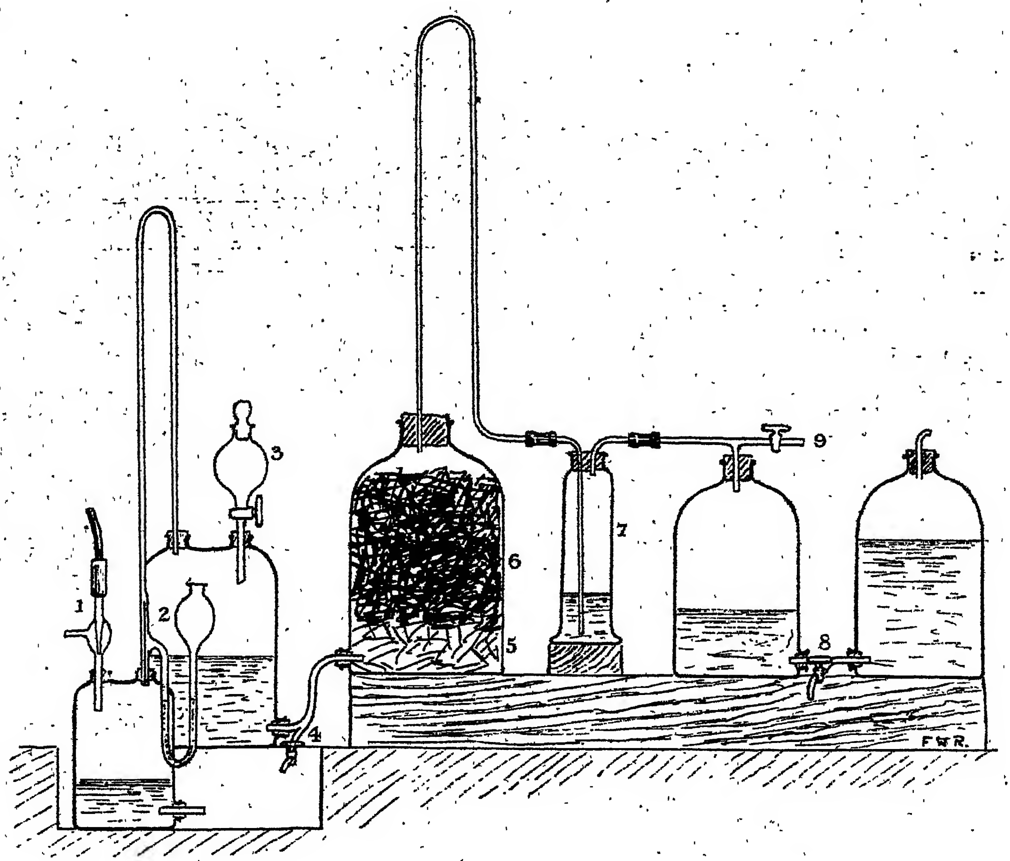
VOL. CIX., No. 2844.

AN IMPROVED SULPHURETTED HYDROGEN APPARATUS.

By FREDERIC WILLIAM RIXON.

THE apparatus described below has undergone a severe test for six months; during that time it has worked most satisfactorily. It possesses certain advantages which will be equally appreciated in laboratories where sulphuretted hydrogen is used constantly or even very intermittently. Some of these advantages may be mentioned.

A larger charge of iron sulphide may be used; the spent acid is easily replaced; when the apparatus is not in use the acid cannot possibly come into contact with the sulphide; the acid is totally enclosed; there is a reservoir of gas; gas and solution can be obtained, and the arrangement is practically *fool* proof.



Description of Apparatus.

Air pressure is obtained by using a filter pump (1) as a blower; too great pressure is relieved by the safety tube (2), which is of wide tubing sealed with water; the height of water in this tube regulates the pressure of gas given by the apparatus.

The air pressure forces acid through the wide tube (4) on to the sulphide (6), a layer of coarsely broken glass (5) acting as a rough filter. The gas is washed (7) and delivered at the tap (9) or stored in the vessels (8), from which the solution may be taken. A tap between 6 and 7 may prove a convenience.

Renewal of acid follows by means of funnel (3) and tap (4). The whole apparatus may be readily fitted up from stock material, and admits of considerable variation to meet different requirements; for large laboratories it can be made to act automatically and deliver gas at a constant pressure, while if occasional supply only is required the apparatus will stand idle without losing efficiency.

The only replacement entailing a partial taking down o the apparatus is the refilling with sulphide.

University of Bristol, April 30, 1914.

Potassium Trioxide and the Stability of Alkaline Peroxides.—R. de Forcrand.—The heat of formation, starting from the elements, of the four alkaline trioxides, Na_2O_3, K_2O_3, Rb_2O_3, Cs_2O_3, is practically the same, viz., +126 cal. The passage from the monoxide to the dioxide disengages quantities of heat which regularly increase from calcium to cæsium:—Ca, 4·11; Li_2, 7·97; Sr, 13·07; Ba, 18·36; Ra, 18·7; Na_2, 19·03; K_2, 22·0; Rb_2, 24·1; Cs_2, 25·0.—*Comptes Rendus*, clviii., No. 14

MOISTURE IN CLOTH.

By WILLIAM M. DOHERTY, F.I.C., F.C.S.

In volume cviii. (August 22, 1913) of the CHEMICAL NEWS there appeared a short article by Mr. E. G. Bryant, B.A., B.Sc., of Port Elizabeth, South Africa, in which is noted the amounts of hygroscopic moisture found in woollen cloth at the above named locality, the said amounts being 12 per cent and 14 per cent respectively. A request for comparison with moisture content of a similar fabric in other parts of the world is expressed, the idea being to see if there are noted differences in "condition" produced by different geographical positions. The subject is perhaps an important one, and I give here my experiences in Sydney, New South Wales. Occasionally during a long period of years I have had to determine the moisture in ordinary woollen cloth, and the results always approximated 10 per cent, which I had considered the normal figure for this part of the world. But as the purpose for which my tests were made was to enable me to calculate analyses results on dry material simply, no notice was ever taken of humidity or temperature of air at the time of making the determinations. Since reading Mr. Bryant's article I have determined the hygroscopic moisture in various kinds of woollen fabrics, noting at the same time the relative humidity and also the temperature of the atmosphere. The method used in expelling the moisture was to heat in a water-oven (98° C.) until constant. The results were as follow:—

Kind of fabric.	Relative humidity. Per cent.	Shade Temp. °F.	Moisture. Per cent.
1. Diagonal serge	57	77	9·81
2. Closely woven worsted	57	77	9·96
3. Coarsely woven tweed	57	77	9·85
4. Berlin wool	60	74	10·00
5. Blanket..	63	75	10·91
6. Closely woven tweed..	89	76	10·93
7. Blanket	85	75	11·50

The degree of humidity seems here to exercise an influence on the moisture content, allowing for the apparent higher hygroscopic quality of the blanket. The amounts in Nos. 6 and 7 were the highest I had yet found, and I re-weighed the pieces after exposure to the air for some days, when the moisture was practically restored. But to obtain this latter result, final weighings had to be made following upon humidity and temperature being identical with those at initial weighings. A further test was made with a piece of high-class blue-back diagonal serge, which consisted of weighing the piece daily, simultaneously noting humidity and temperature. The results were:—

Relative humidity. Per cent	Temperature. °F.	Weight of piece. Grms.
76	77	9·187
89	76	9·214
61	75	9·204
58	74	9·182
49	74	9·176
52	76	9·158
69	77	9·180

Here it will be seen that the greatest humidity does synchronise with the greatest weight. The reverse tendency is also in the appropriate direction, though the figures do not quite coincide. But this lack of absolute coincidence is I think due to lag, which most probably is a disturbing element in such an experiment as I am here describing. I have noticed that some days may elapse (humidity and temperature being equal) before the last amounts of moisture be restored to the dried cloth on simple exposure. The above weighings were made of course under shade conditions wholly, and I found that if the same piece of cloth was exposed to the direct rays of the sun for three hours the weight had fallen to 8·64 grms., that is to say the greater part of the moisture had been expelled.

A final experiment was made during the prevalence of very wet weather, the piece being weighed on a wet day after the rain had been falling more or less continuously for three days. The relative humidity at time of weighing was 90 per cent, and the temperature 77° F. The greatest previous weight was 9·214 grms., and it had now risen to 9·453 grms, an increase of 2·5 per cent. The total percentage of moisture in the cloth on this last occasion was 13·7, thus, during rainy weather, practically reaching the amount found by Mr. Bryant at Port Elizabeth.

Ordinarily, then, the amount of hygroscopic moisture in cloth in Sydney is less than that found by Mr. Bryant in Port Elizabeth. Probably meteorologically the two ports are about on a par as far as this question is concerned.

It should be noted perhaps that these experiments were made in February and March.

Government Laboratory,
Department of Public Health,
Sydney, N.S.W.

FLUIDS WITH VISIBLE MOLECULES.

In a course of four lectures given recently at King's College, London, Prof. Jean Perrin, of the University of Paris, gave an interesting account of his work on the experimental verification of the molecular hypothesis.

The kinetic theory of gases gives an approximate means of determining the actual dimensions of the molecule, and Maxwell obtained an expression for Avogadro's constant N, from considerations connected with the viscosity of gases. The Brownian movement of visible microscopic particles appears to be the result of molecular agitation, and any particle in suspension seems to function as an enormous molecule. If this is so, the gas laws, already extended by van 't Hoff to solutions, must also apply to dilute emulsions composed of equal grains, and if the osmotic pressure of this "gas with visible molecules" is known Avogadro's Law will give the ratio of the masses of the grains to those of the invisible molecule of any gas. In an indefinite vertical column of emulsion in equilibrium the osmotic pressure at any level counterbalances the weight of the higher layers, as in a heavy gas, and the emulsion is a miniature atmosphere. If, then, it is necessary to rise a hundred million times less than in oxygen in order to double the rarefaction, it may be concluded that the visible grain is a hundred million times heavier than the molecule of oxygen. In order to obtain equal grains emulsions made by precipitating alcoholic solutions of resin with water were submitted to a process of fractional centrifugalisation. These emulsions obey the gas laws, and the value of Avogadro's constant N can be calculated from them. It is found that the value of N thus found is independent of the size of the particles, and agrees with the number given approximately by the kinetic theory (68×10^{22}). The Law of Gay Lussac holds good for temperatures between $-10°$ and $+60°$. Since dilute emulsions follow the gas laws it is probable that concentrated emulsions would behave like compressed fluids, and that van der Waals' theory could be applied in studying them. To determine the osmotic compressibility of the emulsion (*i.e.*, the variation of the osmotic pressure as a function of the concentration of the grains) it is necessary to observe the distribution in a vertical column of emulsion, all the grains of which have been counted. The osmotic pressure at each level, supporting all the grains above this level, is thus determined. (The emulsion is its own manometer).

It is then easy to determine whether the pressure P thus obtained satisfies van der Waals' equation—

$$\left(P + \frac{a}{V^2}\right)\left(V - b\right) = RT$$

where R = gas constant.
T = absolute temperature.
V = volume of emulsion containing N grains.
b = four times the volume of these grains.
a = a constant corresponding to the cohesion.

If this is the case the observation of a concentrated emulsion will give Avogadro's number. Experiment verifies this prediction; it is found, however, that the constant of cohesion is negative, and that the grains repel one another to an appreciable distance. This result permits of the experimental determination of the thickness of the double layer of electrification by contact, and throws light upon the properties of colloidal solutions. A knowledge of the compressibility also provides a verification of the theory of Smoluchowski on the spontaneous fluctuations of the density of a fluid in a given volume. The activity of the Brownian movement is defined as the quotient $\frac{E^2}{t}$, where E^2 is the mean square of the displacement in time t. An emulsion should diffuse like a solution of visible molecules with a speed which is greater the greater the speed of the molecules composing it. By calculation it is found that the coefficient D of diffusion is obtained by dividing the activity $\frac{E^2}{t}$ by 6, and since at any level as many molecules pass upward by diffusion as pass downward by gravitation the coefficient of diffusion depends upon the radius r of the grains and the viscosity z. Thus Einstein's equation holds, viz.:—

$$\frac{E^2}{t} = 6\,D = \frac{RT}{N} \cdot \frac{1}{\pi r z},$$

Thus Avogadro's constant can be determined both by measuring the diffusion and by measuring the displacements. In order to study the diffusion emulsions were obtained which were such that the grains remained attached to the walls of the vessel when they came in contact with them. The emulsion thus became progressively weaker by diffusion, and the coefficient of diffusion was given by the increase of the number of grains captured as a function of the time. The displacements of spherules of known radius can be measured very easily, and these measurements, made in very varying conditions as regards the size of the grains and the nature of the intergranular liquid, all gave concordant results for Avogadro's number. Moreover, with relatively large spherules it is easy to measure the rotations, and thus verify Einstein's formula for the Brownian movement of rotation. All these theories apply to granules suspended in a gas, except that Stokes's law no longer holds good. By applying an electric field Townsend's equation for the diffusion of gaseous ions connects the charge e on the granule with Avogadro's number and with the activity of its Brownian movement, viz.:—

$$Ne = \frac{RT}{D}\,\frac{u}{H} = 6\,RT\,\frac{t}{E^2}\,\frac{u}{H}.$$

The verification of these formulæ giving for the product Ne simple multiples of the faraday shows that the charge of microscopic particles is an integral multiple of the same charge (equal to that of the hydrogen ion in electrolysis).

The following table shows the results obtained by the different methods briefly described above:—

	Quotient N/10²².
Viscosity of gases	62
Brownian movement of translation	69
Brownian movement of rotation	65
Fluctuation	60
Electric charge of droplets	65
Radio-activity	{ 62 65

CHEMICAL REACTIONS AT VERY LOW PRESSURES.*

I.—The Clean-up of Oxygen in a Tungsten Lamp.

By IRVING LANGMUIR.

(Continued from p. 246).

Electron Theory of Chemical Combination.

We have seen that the impact between oxygen molecules and tungsten atoms cannot be the determining factor in the reaction of oxygen with hot tungsten. The fact that the velocity of the reaction is not affected by the temperature of the oxygen indicates that the oxygen molecules react primarily with particles of very much smaller mass than themselves, therefore presumably with free negative electrons in the metal.

Since the mass of the electrons is very small, their velocity must be very large in order that they may have the same average kinetic energy as the atoms of tungsten.

From Equation (16) we see that when two particles collide the amounts of impact contributed by each are proportional to $\sqrt{T/M}$. If we consider the impact between oxygen molecules with an average temperature of 298° and negative electrons with velocities corresponding to 1600°, we find that the share of the impact contributed by the oxygen is to that contributed by the tungsten as $\sqrt{298/32}$ is to $\sqrt{1600/0{\cdot}00055}$. That is, the movement of the oxygen molecule is only 1/560 as effective as that of the electron. This difference is so great that we can neglect the velocity of the oxygen entirely in its effect on the reaction.

We have assumed that it is necessary for an electron and an oxygen molecule to collide with an impact exceeding a certain lower limit, in order that chemical combination may ultimately result. Since the velocity of the oxygen molecules is of so little importance, it is simply necessary, for chemical combination, that the electron shall strike the molecule with a velocity which exceeds a certain limit v_0.

Let us now calculate what proportion of the electrons in a metal reach the surface with a velocity exceeding a certain value v_0, and let us determine how this proportion increases as the temperature of the metal increases.

This calculation is identical with that made by Richardson in determining the number of electrons that escape from incandescent metals (*Phil. Trans.*, 1903, cci., 516).

Let N be the number of electrons in each cc. of the metal. Then, according to Maxwell's law, the number dN per cc. which have velocity components perpendicular to the surface of the filament lying between v and $v+dv$ is—

$$dN = \frac{N}{\sqrt{\pi}}\,e^{-(v/a)^2}d(v/a) \quad . \quad . \quad . \quad (19),$$

where—

$$a = \sqrt{2/3}\,\bar{v} \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

Here $\bar{v}$ is the square root of the mean square velocity of the electrons in the metal, and can be calculated by Equation (4)—

$$\bar{v} = \sqrt{\frac{3RT}{M}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1$$

The number of electrons dn with velocities between v and $v+dv$ which reach a unit surface of the metal per second can be obtained by multiplying the number per cc. having this velocity by the velocity component perpendicular to the surface. That is, from (19)—

$$dn = v\,dN = \frac{N}{a\sqrt{\pi}}\,ve^{-(v/a)^2}dv \quad . \quad . \quad (22)$$

* Paper read before the New York Section of the American Chemical Society. From the *Journal of the American Chemical Society*, xxxv. No. 2.

The total number of electrons which reach the surface with a velocity perpendicular to it exceeding a certain value v_0 is therefore—

$$n = \frac{N}{a\sqrt{\pi}}\int_{v_0}^{\infty} e^{-(v/a)^2} v\,dv = \frac{aN}{2\sqrt{\pi}} e^{-(v_0/a)^2} \quad (23).$$

By combining this with (20) and (21) we obtain—

$$n = N\sqrt{\frac{RT}{2\pi M}}\, e^{-Mv_0^2/2RT} \quad . \quad . \quad . \quad (24).$$

The velocity v_0 is the velocity which the electron must have in order that it can combine with an oxygen molecule. As the temperature of the metal varies, the number of electrons having this necessary velocity will increase according to Equation (24). Therefore ε, which measures the rate of the reaction of oxygen with the tungsten, would be proportional to n. We may assume that N and v_0 do not vary with the temperature, and thus obtain from (24) a relation of the form—

$$\varepsilon = B\sqrt{T}\, e^{-b/T} \quad . \quad . \quad . \quad (25),$$

where—

$$b = Mv_0^2/2R \quad . \quad . \quad . \quad (25a).$$

Taking the logarithm of (25), we get—

$$ln\,\varepsilon = -b/T + ln B + \tfrac{1}{2}\,ln\,T \quad . \quad . \quad . \quad (26).$$

Differentiating—

$$\frac{d\,ln\,\varepsilon}{dT} = \frac{b}{T^2} + \frac{1}{2T} \quad . \quad . \quad . \quad . \quad (27).$$

This equation differs from Arrhenius's Equation (11) only by the addition of the term $\frac{1}{2T}$. For all ordinary chemical reactions this term is very small compared to the first term.

The data for ε in Table IV. were compared with this equation. By taking $B = 0{\cdot}85$ and $b = 12830$, Equation (26) gives the results in the fourth column of Table IV. These agree as well with the observed values of ε as do the results in Column 3 obtained from Arrhenius's equation.

We are thus able to derive a correct form of equation for the reaction velocity from Maxwell's distribution law.*

Knowing now the numerical value of b, we can calculate the actual velocity v_0 of the electrons necessary to bring about a reaction. From—

$$v_0 = \sqrt{2bR/M} \quad . \quad . \quad . \quad . \quad . \quad (27a).$$

Substituting $b = 12830$, $R = 83{\cdot}2 \times 10^6$, $M = 0{\cdot}00055$, we find—

$$v_0 = 62{\cdot}4 \times 10^6 \text{ cm. per sec.}$$

This velocity is small compared to that of cathode rays.

It is of interest to know through what voltage drop an electron would have to pass in order so attain this velocity. We have, if P = drop in potential,—

$$P = \tfrac{1}{2}(m/e)v_0^2.$$

For electrons $e/m = 18{\cdot}0 \times 10^6$ e. m. units.

Whence the potential drop is $108{\cdot}0 \times 10^6$ e. m. units or $1{\cdot}08$ volts. It is probably significant that this is the order of magnitude of the voltage necessary to decompose most chemical compounds.

Let us now calculate what proportion of all the electrons reaching the surface do so with a velocity exceeding v_0. If we place $v_0 = 0$ in (24), we find that the total number of electrons reaching the surface is—

$$n_0 = N\sqrt{RT/2\pi M} \quad . \quad . \quad . \quad . \quad . \quad (28).$$

The proportion of these which have a velocity exceeding v_0 is therefore equal to $e^{-Mv_0^2/2RT}$, or, in other words, to $e^{-b/T}$. This ratio is given in Column 3, Table V.

The relative number n/n_0 of electrons striking the oxygen molecules which actually combine with them is very small. For example, if we consider a filament at 1270° being struck by 910 oxygen molecules, we see from the value of ε that on the average only one of these will combine with the tungsten.

TABLE V.

I. Temp.	II. ε observed.	III. n/n_0.	IV. $\varepsilon\, n_0/n$.
1270° K	0·0011	0·000041	27
1470	0·0053	0·000162	33
1570	0·0094	0·000282	33
1770	0·0255	0·000715	36
2020	0·049	0·00173	28
2520	0·12	0·0062	19

On the other hand, we see from the value of n/n_0 that in order for one electron to combine with an oxygen molecule $1/0{\cdot}000041$ or about 24,400 electrons must collide with oxygen molecules without combining. This leads us to the conclusion that each oxygen molecule striking the filament will, on the average, be struck by about 27 electrons. The number of electrons striking each oxygen molecule is equal to $\varepsilon n_0/n$ in the fourth column. The average is about 30, and up to 1800° does not vary much with the temperature.

The number of electrons which strike each oxygen molecule depends on the number of electrons per unit volume in the metal, on their velocity, and on the forces the electron has to overcome in moving from the interior of the metal to the point where it collides with the oxygen molecule. If we assume that these forces are negligible, we may roughly calculate the number of electrons per unit volume.

Let us assume provisionally that the average distance between the electrons in the metal is about the diameter of an oxygen molecule. Since there are six possible directions perpendicular to each other in which an electron may move, we may consider that only one-sixth of all the molecules are moving towards the surface at any one time. If the velocity of the electrons and oxygen molecules were the same, then the chance that an electron would strike a molecule during a collision of the latter with the metal would be one sixth. We can therefore readily see that the number of electrons which would strike the oxygen molecules during a single collision would be equal to $1/6v_2/v_1$, where v_2 is the average velocity of the electrons and v_1 the average velocity of the oxygen molecules. The mass of an oxygen molecule is about 58,000 times as great as that of an electron. If the temperature of the oxygen and metal were the same, the velocity of the electrons would be $\sqrt{58{,}000}$ or 240 times that of the molecules. As the temperature of the oxygen is lower than that of the metal, this ratio would be somewhat larger—probably in the neighbourhood of 400. In this case $1/6v_2/v_1$ becomes 67. This represents the number of electrons which would strike an oxygen molecule if the average distance between the electrons in the metal were equal to the diameter of the oxygen molecule. The atomic volume of tungsten is about one-third of the molecular volume of oxygen. If we should assume there is one free electron for each atom of metal, then we should expect 3×67 or 200 electrons to strike each oxygen molecule during a collision. The results of our experiments have already led us to conclude that the number of collisions is about 30. This would indicate that there are about one-seventh as many free electrons as there are tungsten atoms. It must be remembered, however, that this conclusion has been reached by assuming that no work is required to move an electron from the interior of the metal to the surface where it can collide with the oxygen molecule. If such forces do exist opposing this motion, then there must be more than one-seventh as many electrons as tungsten atoms. In any case, it is significant that we find the number of electrons so nearly equal to that of the tungsten atoms.

The question arises as to whether the impact from a smaller number than 30 electrons might not be sufficient to drive away an oxygen molecule. The momentum of a

molecule moving with a velocity corresponding to the temperature T is proportional to $\sqrt{MT}$. If we take the momentum of the electrons in the metal at 1600° as unity, we find for the momentums of—

Electrons in metal	1
Tungsten atoms in metal	570
Oxygen molecules at 300°	100
Oxygen molecules at 1600°	240

The average momentum taken up by the oxygen is 100+240 or 340. The collision of one electron against an oxygen molecule is only capable of giving it the momentum $2\times1=2$. It would require, therefore, the impact from 170 electrons to give the oxygen molecule the velocity it must have when it leaves the surface of the metal. This would indicate that about 85 per cent of its momentum is obtained by impact against tungsten atoms and only about 15 per cent from collisions with electrons.

We see, then, that our conclusion that each oxygen molecule is struck by 30 electrons, does not lead us into any inconsistencies, but leads to results which are in themselves probable.

(To be continued).

THE SCIENTIFIC WEEK.

(From Our Own Paris Correspondent).

The Vulcanistion of Rubber by the Ultra-Violet Rays.

Prof. Dastre, Member of the Academy of Sciences, in the names of Messrs. André Helbronner and Gustave Bernstein, has communicated a paper concerning the vulcanisation of rubber solutions by ultra-violet rays. The action of these rays on solutions of rubber to which sulphur has been added produces a combination between these two bodies without, however, the rubber, although vulcanised, being precipitated from the solutions. Contrary to what might be expected, remarkably stable solutions are thus obtained, and these solutions give, by evaporation, a perfectly insoluble pellicule. The analysis of the phenomenon enables one to follow, step by step, the process of vulcanisation. The ultra-violet rays do, indeed, precipitate the sulphur and depolymerise the rubber. These are two concomitant actions, combined with the repolymerisation of the rubber under the action of the sulphur, which constitute the vulcanisation of which the intimate nature is thus revealed, and completely confirms the theories already expressed by one of the authors. If we pass now to the practical side of the matter, the solutions vulcanised by the ultra-violet rays have an interesting future before them. They enable all kinds of repairs to be effected for any object in rubber. A veritable autogenous soldering is thus obtained of this matter, resisting heat or any other mechanical action, and it thus becomes unnecessary to perform an ulterior vulcanisation, which long and delicate operation was before obligatory. It is then quite a little revolution for all repairs, and especially that of rubber tyres. This interesting discovery will also have most important applications in the industry of rubber clothes, of envelopes of dirigible balloons, of shoes, &c.

Microbian Droplets.

M. Roux has summed up the works of M. Trillat, of the Pasteur Institute, and M. Tanassier, concerning the formation of microbian droplets in the atmosphere and their properties. The authors have first shown that microbes can play the *rôle* of a nucleus for the condensation of humidity in the air, which explains the presence of numerous microbian drops, which are so much the lighter as the germ inclosed is smaller. The speed of the fall of these droplets follows the law of Stokes. MM. Trillat and Tanassier have studied the action of cooling on these microbian droplets. Whereas the total cooling of a microbian mist, like that of a sudden decompression, has the effect of resolving the drops into rain and of purifying the atmosphere, the lowering of the temperature of one point of a microbian atmosphere determines an immediate transport of the germs that assemble and are localised in the cooled regions. The case is striking for the cooling surfaces. The knowledge of these results throws some light on the transmission of certain diseases by the intermediary of microbian droplets. Perhaps, in the future, some applications may be made for the purification and salubrity of rooms, halls, hospital wards, &c.

Musical Sensation.

Very curious experiments, especially interesting to musicians, have just been made by Dr. Marage. In a recent study he had shown that for each vowel there exists a note on which a minimum of energy is necessary to make it heard; that is, indeed, the origin of the telephonic "allo." Dr. Marage, in a paper presented before the Academy of Sciences by Prof. d'Arsonval, studies the sensibility of the ear for certain musical sounds. The question was to know the impressions experienced by an audience composed of musicians, savants, literary men, and society people, while listening to the same pieces of music of the sixteenth and seventeenth centuries, performed successively on the piano and on instruments of the period: clavecin, clavicord, lute, and viol. To realise this experiment the three hundred pupils who follow the classes at the Sorbonne of the physiology of speech and singing have been divided into two series. The pupils were to note their physiological and musical impressions. Out of an audience of 300 only 142 copies were given in; that is to say, that over 50 per cent of the pupils had no impressions or did not wish to write them down. And yet the copies were anonymous. The other half, however, on the contrary, experienced very diverse sensations. The pupils who gave in their copies were divided into 51 professional musicians or singers—25 cultivated persons, that is to say, with a good knowledge of music and studying it from a taste of the same, 34 with no musical knowledge, 13 scientific persons, professors, pupils of the Polytechnic School, of the Central School of Civil Engineers, or of the Sorbonne, and 19 literary professors or pupils. The copies, judged from the point of view of the analysis of the sensations, have given the following results:—The cultivated come out at the top of the list with 77 per cent of good copies; professors of singing and music come next with 62 per cent. The scientific pupils are greatly superior to the literary; 47 per cent of the first against 35 per cent of the second gave in excellent copies. The literary people make long descriptions, interesting and agreeable to read, but it is often difficult to discover what are the sensations they experience. The scientific, on the contrary, have clear ideas expressed in a few lines. Concerning the physiological impressions, it is to be remarked that almost all the audience is at first disagreeably impressioned by the thin and metallic sounds of the clavecin, then the ear gradually gets used to these chords, new to it, and then it finds in them certain qualities. The grave sounds of the viols are immediately agreeable to the audience. M. Marage draws a practical and interesting consequence from these impressions; since grave sounds are agreeable to the ear and shrill sounds are disagreeable, motor-cars ought to have two sorts of trumpets; one with grave sounds for towns, not to be heard at a great distance, so as not to tire the citizens, and the other with a shrill sound that can be heard from afar, irritating the ear and forcing the peasants to pay attention. A curious phenomenon of suggestion has also been observed by M. Marage. After a first performance it was decided to change the piano. The instrument was new, and it had been thought that the sounds it gave forth were not very harmonious. Twenty musicians had expressed the desire to be present at the second series, at which the same programme was to be performed. They all noted down that

the new piano was very superior to the first one. Now, for some reason unknown to M. Marage, the instrument had not been changed, and was the same at both series. To sum up, Dr. Marage wonders if musical critics are not often influenced by the special dispositions of their auditive nerves. The particular action of vibrations on each nervous system, the habit of hearing certain sounds, and, lastly, the previous education, must deprive the artistic criticism of the value possessed by the scientific criticism. But, as Dr. Marage observes, these are important questions which can only be touched upon in passing.

A New Sounding Apparatus.

The Prince of Monaco has presented before the Academy of Sciences a new sounding apparatus invented by M. Alphonse Berget, Professor at the Oceanographic Institute. This apparatus is based on the measure of pressure; it thus gives results that are independent of the curve that the sound line may take during its descent. It is based on the compression of a volume of water in a glass reservoir terminated by a slender tube, divided and coated with silver in the inside. An index of mercury, forming a piston, eats away the silvering as far as the point where it stops, so that when the instrument is drawn up it is possible to read the maximum pressure reached; that is to say, the depth. The indications of the apparatus graduated experimentally by the hydraulic press have only one correction, that of the temperature, which is made according to the table of Amagat; the depths that it measures are exact or only vary about 10 metres; that is to say, about an atmosphere.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, May 14, 1914.

Sir William Crookes, O.M., President, in the Chair.

Papers were read as follows:—

"*Various Inclinations of the Electrical Axis of the Human Heart. Part I.A. The Normal Heart. Effects of Respiration.*" By Dr. A. D. Waller, F.R.S.

"*Fossil Plants Showing Structure from the Base of the Waverley Shale of Kentucky.*" By Dr. D. H. Scott, For. Sec. R.S., and Prof. E. C. Jeffrey.

"*Controlling Influence of Carbon Dioxide in the Maturation, Dormancy, and Germination of Seeds.*" Part II. By F. Kidd.

The inhibitory effect of carbon dioxide on the germination of seeds previously described is dealt with in relation to temperature and oxygen supply. In relation to temperature the result obtained is unusual, the inhibitory action being more pronounced at low temperatures than at high. At 3° C. complete inhibition was obtained with 4 per cent CO_2; at 17° C. as much as 24 per cent had to be employed to obtain the same result. Varying partial pressures of oxygen also effect the inhibitory action of carbon dioxide, but to a less degree than temperature. Thus with 5 per cent oxygen, 15 per cent CO_2 produced inhibition; with 20 per cent oxygen, 27 per cent CO_2 was necessary. The author emphasises the fact that the adjustments of the moist seed by which it is enabled to continue dormant in the presence of oxygen and water, rather than those of the dry seed, are likely to have formed the central problem of seed life in nature. A low temperature and a decreased oxygen supply are often the natural conditions of a seed's environment in the soil.

Attention was called to the condition of restrained growth and to the non-sprouting of the embryos of many seeds while coming to maturity on the parent plant. The actual CO_2 content of the tissues of such seeds is compared with that of similar seeds while actually sprouting. It seems probable that here also we may be dealing with an effect of carbon dioxide inhibition. Neither lack of water nor physiological insufficiency can account for the non-germination of the maturing embryos in the cases described.

In small amounts carbon dioxide is found to have a stimulatory effect on germinating seeds. The vitality of certain short-lived seeds is found to be prolonged under the influence of CO_2. Seeds of the rubber tree (*Hevea Brasiliensis*) treated in this way outlived those kept in commercial packing.

Correlating the results obtained in this and in a former paper, the author strongly emphasises the controlling influence of carbon dioxide in the biology of seeds. It appears that the normal resting stage of a seed is primarily a phase of narcosis.

"*Cultivation of Human Tumour Tissue in vitro.*" By D. Thomson, M.B., and J. G. Thomson, M.B.

"*Nutritive Conditions Determining the Growth of certain Freshwater and Soil Protista.*" By H. G. Thornton and G. Smith.

Experiments made on the growth of *Euglena viridis* in artificial media showed that, in addition to those inorganic constituents necessary for the growth of a green plant, which were supplied by Miguel's formula for growing Diatoms, a certain quantity of organic material, *e.g.*, infusion of hay, was necessary. In order to determine the constituent in this organic material which stimulated growth, various pure substances, such as carbohydrates, tartaric acid, saccharin, allantoin, peptone, and various amido acids, were used in dilute solutions. Of these, only very weak solutions of amido acids favoured a really strong growth, the most favourable substances being tyrosin and phenyl-alanine which are very slightly soluble in water. In stronger solutions of alanine and glycocoll, bacterial growth interfered with the culture of Euglena. Tyrosin in the proportion of 1 in 24,000 gave an optimal growth, a fact which suggests that the amido acid acts as an auxiliary or stimulant rather than as the main source of nutrition.

Experiments with soil flagellates, especially *Prowazekia terricola* (Martin), showed that they could be cultivated in many solutions in which bacteria flourished, the flagellates feeding on several different kinds of bacteria.

Samples of various types of soil and water were tested for the presence of bacterial-feeding flagellates, and these were found in all the samples, being most abundant in highly-manured soil. The wide distribution and abundance of these soil flagellates, and their very rapid growth in the presence of bacteria, suggests that they are of importance in the economy of the soil.

CHEMICAL SOCIETY.

Ordinary Meeting, May 7, 1914.

Prof. W. H. Perkin, LL.D., F.R.S., President, in the Chair.

Certificates were read for the first time in favour of Messrs. Alfred Archibald Boon, D.Sc., Heriot-Watt College, Edinburgh; John Vernell Cutler, Rose Cottage, Farringdon Lane, Ribbleton, Preston; Galstaun Shanazar Galstaun, B.A., Abbotsholme, Derbyshire; James Mylam Gittins, M.Sc., South Lynn, Limes Road, Folkestone; Alfred Holt, 32, Britain Street, Bury; John Cyril Jennings, Rosindell, Fairlop Road, Leytonstone, N.E.; Hashmat Rai, B.A., M.Sc., Chemical Buildings, Government College, Lahore, India; Frederic Robinson, M.Sc.Tech., The Hollies, Mile End, Stockport; Walter Edward Rowbottam, 23, Darville Road, Stoke Newington, N.; Alfred John White, B.Sc., Hawes Down, West Wickham, Kent.

Messrs. W. Sloan Mills and P. C. Austin were elected

Scrutators, and a ballot for the election of Fellows was held. The following were subsequently declared as duly elected:—Abdel Hameed Ahmad, B.Sc.; Charles Frank Armstrong; Raymond Foss Bacon, B.Sc., M.A., Ph.D.; Arthur Baxter, B.Sc.; Frederick Stanley Baxter; Robert Reginald Baxter, B.A.; Charles Wesley Bayley; Robert Odell Bishop; Edward Godfrey Bryant, B.A., B.Sc.; Albert Coulthard, B.Sc., Ph.D.; Robert Barclay Craig; Robinson Percy Foulds, M.Sc.; Hugh Miller Galt, B.Sc., M.B., D.P.H.; Brojendranath Ghosh, M.Sc.; Clifford Girdlestone Gill; Alfred Cornwall Harrison; Richard Selwyn Haskew; Jaroslav Heyrovsky, B.Sc.; Arthur Bertram Hobson, M.Sc.; Trevor Edward Hodges; Lawson John Hudleston; Ralph Waldo Emerson MacIvor; Birendranath Maitra, M.Sc.; Yusuf Ismail Mulla; William Whalley Myddleton, M.Sc.; Arthur Ulysses Newton, B.Sc.; James Riddick Partington, B.Sc.; Walter Ryley Pratt, B.Sc.; Henry Ratcliffe; Walter William Reeve, B.Sc.; Herbert Corner Reynard, B.Sc.; John Rogers; Perby Charles Rundell; Lall Behary Seal; Max Herbert Tagg, B.Sc.; Norman Cecil White, B.A., B.Sc.; Albert Watkins Maggs Wintle.

Of the following papers those marked * were read:—

*115. "*Researches on Santalin.*" Part II. By JOHN CANNELL CAIN, JOHN LIONEL SIMONSEN, and CLARENCE SMITH.

As a result of determinations of the molecular weight of certain derivatives of santalin by Barger's method, the authors are of the opinion that the formula previously assigned to this colouring matter should be doubled, and hence should be $C_{30}H_{28}O_{10}$.

The presence of four benzene rings in the santalin molecule appears also to be indicated by the facts that (1) the monomethyl ether yields, on oxidation, a mixture of anisic and veratric acids, and (2) nitrosantalin dimethyl ether yields four different benzenoid acids on oxidation.

Santalin yields anthracene on distillation with zinc dust (Grandmougin), and the authors suggest that it is probably a dianthracene derivative.

DISCUSSION.

Dr. TURNER suggested that the low molecular-weight values found for santalin in phenol might be due to combination with the solvent. Of the other solvents employed, ether was most likely to lead to the simplest (or normal) molecular weight.

*116. "*The Nature of Molecular Association. Its Relation to Chemical Combination.*" By WILLIAM ERNEST STEPHEN TURNER and SOLOMON ENGLISH.

The term "association" is frequently used to denote both the phenomenon of the formation of complexes of similar molecules and of dissimilar molecules (formation of molecular compounds). Further, views have been expressed to the effect that the formation of molecular compounds is a natural consequence of molecular association in the component substances.

In order to test how far these views are truly founded, the subject was investigated by a review of the different classes of substances which form molecular compounds and by an investigation of the behaviour in benzene, bromoform, chloroform, and water of mixtures of (1) alkyl and aryl haloids, (2) associated organic substances, (3) associated organic substances and alkyl or aryl haloids, (4) salts, (5) salts and alkyl or aryl haloids, (6) salts and associated organic substances, (7) alkyl or aryl haloids and iodine, (8) salts and iodine, (9) associated organic substances and iodine. A study was also made of the mixture of α-naphthylamine and phenol, in which combination is known to occur.

It was shown that whilst associated substances have a marked tendency to form molecular compounds, mixtures of associated substances can often be obtained without chemical combination, and, on the other hand, molecular compounds are also produced by non-associated substances.

Mixtures of salts in bromoform, so far from dissociating each other, actually produce increased association. In one or two cases investigated the increased association passes through a maximum at a certain concentration, and then diminishes to zero. Similar behaviour is found in chloroform, and also in water, but in the latter to a less extent.

Benzoic and acetic acids have but little effect on one another, but in some other cases of organic associated substances, each constituent influences the other, probably by combination.

Alkyl or aryl haloids and iodine, and organic associated substances and iodine have but little effect on one another; a nitrate in bromoform solution acts with iodine to some extent, but not nearly so much as chlorides, bromides, and iodides, which form periodides, these in turn apparently becoming associated.

*117. "*The Action of Diastase on Starch Granules.*" Part I. By JULIAN LEVETT BAKER and HENRY FRANCIS EVERARD HULTON.

Brown and Morris (*Trans.*, 1890, lvii., 510) have stated that when precipitated malt diastase is allowed to act at the ordinary temperature on the granules of barley starch, the whole of the optically active substance produced is maltose. Later Morris (*Trans.*, 1901, lxxix., 1085) confirmed the observation in the case of malt extract, but when precipitated diastase was used a smaller yield was obtained, and the product was stated to consist of a mixture of maltose and dextrin. No experimental evidence was adduced in support of this assertion.

The authors bring forward experimental evidence to show that the similarity to maltose of the specific rotatory power and the cupric reducing power of the products so formed at temperature varying between 15·5 and 37·5 is fortuitous.

On submitting the products of such action to fermentation, alcoholic fractionation, and dialysis, a dextrin was isolated which had a molecular weight exceeding 1500, an $[\alpha]_D$ of 177°, and a cupric reducing power varying between 11 and 20 per cent of maltose. This dextrin, which is not identical with the "stable dextrin" of Brown and Millar (*Trans.*, 1899, lxxv., 315), constitutes about 1/5th of the conversion products, from which crystalline maltose was also isolated, and a dextrin or dextrins of the same molecular weight and optical activity as maltose, but of much lower cupric reducing power. When the time of conversion exceeds three or four days dextrose is produced.

DISCUSSION.

Dr. PLIMMER pointed out that French observers consider that starch granules consist of two constituents.

The formation of small quantities of dextrose by the action of malt diastase might arise from one of these two constituents, and not from the other, which yields only maltose on hydrolysis.

In reply, Mr. BAKER said that he did not think that Maquenne and Roux's differentiation of the starch granule into amylocellulose and amylopectin affected the question of the formation of dextrose. If the dextrose were derived directly from one or other of these substances, it would be reasonable to expect its production at once, but the experimental evidence was against this. It was more probable that the dextrose was formed by the slow hydrolysis of some of the dextrins of low molecular weight present in the conversion products.

*118. "*The Atomic Weight of Lead from Ceylon Thorite.*" By FREDERICK SODDY and HENRY HYMAN.

Recent results in radio-activity suggest that the lead derived from a mineral rich in thorium and poor in uranium may have an appreciably higher atomic weight than that of ordinary lead. If the end products of both uranium and thorium are, as is supposed, the isotopes of lead, the former should have an atomic weight of 206 and the latter of 208·4, whilst the accepted value for ordinary lead is 207·1. Ceylon thorite is uniquely suited for an experimental test of the question. The original analysis (W. R.

Dunstan, *Ceylon Mineralogical Survey Report*, March 31, 1904) gave 58·24 per cent of thorium, 0·38 per cent of uranium, and no lead. The authors' analysis gave 0·35 per cent of lead and 54·5 per cent of thorium. Whereas the chemical estimation of the uranium gave 0·72 per cent, a later preliminary estimation of the radium by the emanation method showed more uranium, namely, 1·6 per cent, and this is probably the more accurate. Owing to its greater rate of change, uranium will be about three times as effective in producing lead as thorium, so that if the lead in Ceylon thorite is entirely of radio-active origin, and if both isotopes are stable, the atomic weight should be 208·2.

Rather more than a grm. of the finally purified lead chloride was obtained from about a kilogrm. of the mineral, and used in the determinations. Exactly similar estimations with it and with ordinary lead chloride, purified by an identical series of processes, have shown that the thorite lead has distinctly the higher atomic weight. The determinations are purely relative, the atomic weight of ordinary lead being taken as 207·1. The method adopted followed, in part, that of Baxter and Wilson. The lead chloride was fused in hydrogen chloride before weighing, and its solution titrated with silver nitrate solution, the end-point being determined without an indicator by the cloud method. Two separate determinations showed a difference of between 0·4 and 0·5 per cent in the volumes of the silver nitrate solution required by equal weights of the two chlorides, whereas the errors of the estimation do not probably exceed 0·1 per cent. The relative atomic weight of the thorite lead calculated from the results is 208·4. The determinations so far carried out do not suffice to settle the question, but they show clearly a difference in the expected direction of the right order of magnitude.

From a preliminary examination with the Féry spectrograph, the spark spectra of the two specimens of lead, between 6656·3 and 2170, appear to be identical, except for the line 4760·1, which is much weaker in the thorite lead than in ordinary lead.

*119. "*A Criticism of the Hypothesis that Neutral Salts Increase the Dissociation of Weak Acids and Bases.*" By JAMES WILLIAM MCBAIN and FREDERICK CHARLES COLEMAN.

It was shown that if the hypothesis of Acree, Bredig, Snethlage, &c., is accepted, namely, that undissociated hydrochloric acid catalyses the inversion of sucrose better than hydrogen ion, and if, further, the data of A. A. Noyes and his collaborators are employed, not only do the data of Arrhenius (1899) for the acceleration caused by adding a neutral salt to a weak acid fail to prove that the dissociation-constant of the weak acid is enhanced by the presence of the neutral salt, but they may even be adduced as strong evidence against the existence of such an effect.

It was further pointed out that much of the evidence brought in support of the enhancement hypothesis is derived from methods often subject to grave systematic errors, involving, for instance, colour changes in colloidal or electrolytic colloidal systems, or distribution data—methods which are known in some cases to give highly distorted results. Here the results are conflicting in order of magnitude, and even in sign. The evidence of the electromotive-force measurements is also unfavourable to the hypothesis.

The authors conclude, therefore, that on the whole there is no experimental evidence for the supposed increase in the dissociation-constant of weak acids and bases caused by the presence of neutral salts.

120. "*Studies in Substituted Quaternary Azonium Compounds containing an Asymmetric Nitrogen Atom.* Part II. *Resolution of Phenylbenzylmethylazonium Iodide into Optically Active Components.*" By BAWA KARTAR SINGH.

The author, in continuation of his work (*Trans.*, 1913, ciii., 604), has prepared externally compensated phenylbenzylmethylazonium iodide by two different methods, namely, (i.) by the action of methyl iodide on phenylbenzylhydrazine, and (ii.) by the action of benzyl iodide on phenylmethylhydrazine. In the second reaction there is also produced, owing to substitution having taken place, benzyldimethylazonium iodide, $(C_7H_7)(CH_3)_2(NH_2)NI$.

The resolution was effected with the aid of *d*-camphor-β-sulphonic and *d*-α-bromocamphor-β-sulphonic acids. In each case the first fractions consisted of pure *d*B*d*A component; in the last fractions the two component salts *d*B*d*A and *l*B*d*A formed solid solutions. The *l*B*d*A component could not therefore be obtained in a pure state, and the process of resolution was very slow and partial.

No mutarotation was observed in the case of any of the compounds obtained.

Several salts of the externally compensated and optically active azonium base were described.

121. "*Contributions to the Chemistry of the Terpenes.* Part XVII. *The Action of Hypochlorous Acid on Camphene.*" By GEORGE GERALD HENDERSON, ISIDOR MORRIS HEILBRON, and MATTHEW HOWIE.

When treated with dilute aqueous hypochlorous acid camphene gives a quantitative yield of a *chlorohydrin*, $C_{10}H_{16}Cl\cdot OH$, a crystalline solid, m. p. 93°. This compound reacts readily with aqueous or alcoholic alkalis, yielding *iso*camphenilanaldehyde, and by the action of phosphorus pentachloride is converted into camphene dichloride, $C_{10}H_{16}Cl_2$. *iso*Borneol is obtained by the action of zinc and alcohol on the chlorohydrin, which therefore is a chloro*iso*borneol. On oxidation with chromium trioxide the chlorohydrin is converted into a crystalline *chloroketone*, $C_9H_{15}Cl{:}CO$, m. p. 132°, which gives camphor when heated with zinc and alcohol.

122. "*Reactions by Trituration.*" By LESLIE HENRY PARKER.

It has been shown by Carey Lea (*Phil. Mag.*, 1892, [v], xxxiv., 46; 1893, xxxvi., 351; 1894, xxxvii., 31, 470) that shearing stress is capable of "disrupting the molecule" of many endothermic compounds, being far more efficient in this respect than simple pressure of enormous magnitude. This fact, combined with the results of Spring's work on the sulphates and carbonates of sodium and barium (*Bull. Soc. Chim.*, 1885, [iii.], xliv., 166; 1886, xlvi., 299), was the cause of the present investigation into the interaction of various salt pairs, presumably in the solid state, by trituration.

Various pairs of salts were thoroughly dried, and ground together in a dry atmosphere. In most cases mutual action took place very easily, but not always. It was noticed that those substances which reacted most easily under the pestle were those which were easily fusible in ordinary circumstances, and *vice versâ*, and the author arrives at the same conclusion as Johnston and Adams (*Am. Jour. Sci.*, 1913, [iv.], xxxv., 205), that shearing stress, or "non-uniform" pressure, causes local or surface fusion of the substance to which it is applied.

It can also be shown that the action of shearing stress is fundamentally different from that of simple pressure, the chief difference lying in the fact that the products of any reaction occasioned by shearing stress are not necessarily denser than the reacting substances. Experiments have also been conducted with the object of determining whether the trituration caused any ionisation of the atmosphere round the ground substances, but without success.

123. "*The Reaction between Dilute Acid Solvents and Soil Phosphates.*" By JAMES ARTHUR PRESCOTT.

The author has investigated the action of dilute acid solvents on soil with respect to the amount of phosphoric oxide extracted. The extractions were made at constant temperature for varying lengths of time, and with initial concentrations of from 0·06 to 0·2 equivalents of acid per litre.

The amount of phosphoric oxide extracted is approximately proportional to the initial strength of the extracting acid. With nitric, hydrochloric, and sulphuric acids, an

increase in the time of extraction brings about a decrease in the amount of phosphoric oxide extracted. With citric acid the reverse is the case.

The amount of acid neutralised by the soil increases with the time of extraction, but an excess of acid always remains, large in proportion to the amount of phosphoric oxide present. The greatest diminution in the quantity of phosphate extracted with increase in time of extraction occurs with soils containing the highest proportion of clay. It is difficult to account for the removal of the phosphoric oxide from the solution on chemical grounds in view of the large excess of acid present, and the phenomena were therefore studied from the point of view of adsorption.

The results obtained by Hall and Amos (*Trans.*, 1905, lxxxix., 205) were found to agree with the adsorption relationship established by Freundlich, $Y/M = KC^{1/p}$, where Y = amount adsorbed by a quantity M of adsorbent, and C = equilibrium concentration of the solution.

For the Saxmundham soil $p = 0.58$; for the Broadbalk soils (5 and 8) $p = 1.63$; for the Hoos soil (2AA) $p = 1.414$.

In these results, a correction has to be made for the amount of phosphate still left in the soil.

The author has further investigated this point by adding known amounts of phosphate to a soil, and the curves obtained led to the conclusion that the amount of phosphate originally present in the soil, and soluble in hydrochloric acid, was the same as that soluble in citric acid.

For a soil from Agdell field, which had already been extracted twice with dilute acid, p was found to be 1.96 for hydrochloric acid, 0.06 equivalent per litre, and 0.485 for citric acid of the same acidity.

The same soil was also extracted seven times in succession with 2 per cent sodium hydroxide, and was found to contain no phosphate soluble in dilute acid solvents. Adsorption experiments could therefore be carried out without any correction whatever. The Freundlich law was found to hold, giving a value of $p = 2.22$ for hydrochloric acid and 2.08 for citric acid.

124. "*Influence of the Dilution of Hydrogen Peroxide on the Velocity of Precipitation of Manganese from Ammoniacal Solutions in Presence of Zinc.*" By Andrew Jamieson Walker and Walter Farmer.

A study of the effect of dilution of the hydrogen peroxide on the accuracy of the results obtained in Jannasch's method for the separation of manganese and zinc in ammoniacal solution has shown that with a time-limit of thirty minutes precipitation of the manganese as $MnO(OH)_2$ is complete with solutions of hydrogen peroxide of 2.5 per cent strength. More concentrated solutions of the peroxide, up to 6 per cent, are equally efficacious. When the concentration is below 2.5 per cent, the manganese is not completely precipitated within the time indicated, the percentage error increasing in a marked degree with increase in the dilution. With such dilute solutions the manganese is precipitated as carbonate along with the zinc, so that under these conditions the percentage results obtained for zinc are too high. The influence of the dilution can be graphically represented by plotting curves with the percentages of hydrogen peroxide as abscissæ, and the percentage yields of mangano-manganic oxide and of zinc carbonate as ordinates.

The table gives the results obtained in a series of nine experiments. 0.4142 grm. of $MnSO_4,4H_2O$ should give 0.1417 grm. of Mn_3O_4, and 0.4142 grm. of $ZnSO_4,7H_2O$ should give 0.1806 grm. of $ZnCO_3$. This quantity of the salts was employed in each determination. The experimental error is much magnified by translation into percentage yield.

The zinc carbonate precipitated in the 6—2 per cent separations was quite white. As the dilution was increased, it developed a distinct light brown tint, due to the presence of manganese. Within the limits of experimental error, the deficiency in the percentage yields for manganese is balanced by the excess in the corresponding yields for zinc.

Percentage strength of H_2O_2.	Mn_3O_4. Grm.	Percentage yield of Mn_3O_4.	$ZnCO_3$. Grm.	Percentage yield of $ZnCO_3$.
6.0	0.1411	99.59	0.1815	100.53
5.0	0.1410	99.51	0.1815	100.53
4.0	0.1410	99.51	0.1815	100.53
3.0	0.1410	99.51	0.1816	100.59
2.0	0.1409	99.42	0.1817	100.61
1.0	0.1381	97.51	0.1861	103.99
0.75	0.1345	94.93	0.1915	105.99
0.5	0.1297	91.56	0.1995	110.49
0.3	0.1151	81.25	0.2206	122.19

The results indicate that in the separation of manganese and zinc in ammoniacal solution, hydrogen peroxide of not less than 2.5 per cent strength can be employed with satisfactory results (compare Jannasch and MacGregory, *Journ. Prakt. Chem.*, 1891, [ii.], xliii., 402; Jannasch and Niederhofheim, *Ber.*, 1891, xxiv., 3945; Jannasch and von Cloedt, *Zeitsch. Anorg. Chem.*, 1895, x., 405; Jannasch and Lehnert, *Ibid.*, 1896, xii., 134; Jannasch, "Gewichtsanalyse," Leipzig, 1897, 43).

125. "*Additive and Substitutive Compounds of Mercuric Nitrite with Organic Thio-derivatives.*" Part I. By Prafulla Chandra Ray.

Mercuric nitrite yields with methyl and ethyl mercaptans compounds of the type $(R{\cdot}S{\cdot}HgNO_2)_2,Hg(NO_2)_2,H_2O$, where R represents an alkyl group. With the substituted carbamides it forms compounds of the general formula— $NHR{\cdot}C(:NH){\cdot}S{\cdot}HgNO_2,2HgS,HgO$; with thioacetamide and benzamide, nitrites of the type—

$$CR(:NH){\cdot}S{\cdot}HgNO_2,HgS,HgO$$

(R = alkyl or aryl); and with thicacetic acid a salt of the formula $CH_3{\cdot}CO{\cdot}SH,Hg(NO_2)_2,HgS,HgO$. The compound with thiosemicarbazide has the formula $2NH_2{\cdot}NH{\cdot}C(:NH){\cdot}S{\cdot}HgNO_2.HgO,H_2O$, and that with dithiocarbamic acid $NH:C(S{\cdot}HgNO_2)_2,HgS$.

With the thiocarbimides, also, compounds having the general formula $R{\cdot}N:CS{\cdot}Hg(NO_2)_2,2HgS,HgO$ have been obtained; that with ethyl thioether has the formula $2Et_2S,3Hg(NO_2)_2$. It is found that whenever a thio-compound tautomerises giving the thiol group [for example, $CH_3{\cdot}CS{\cdot}NH_2 \rightarrow CH_3{\cdot}C(SH):NH$] the first reaction is as follows:—

$$\cdot SH + Hg(NO_2)_2 = \cdot S{\cdot}HgNO_2 + NHO_2.$$

126. "*The Reactivity of Antimony Haloids with Various Types of Unsaturated Compounds.*" Part I. By Ernest Vanstone.

The eight binary systems formed by *s*-diphenylethane (dibenzyl), stilbene, azobenzene and benzil, and antimony trichloride and tribromide respectively have been investigated by thermal analysis.

s-Diphenylethane forms the compounds, $4SbCl_3,C_{14}H_{14}$, $2SbCl_3,C_{14}H_{14}$, and $4SbBr_3,C_{14}H_{14}$.

Stilbene forms the compounds $2SbCl_3,C_{14}H_{14}$ and $2SbBr_3,C_{14}H_{14}$.

The compounds with *s*-diphenylethane are stable; those with stilbene are unstable, and difficult to obtain. The tendency is to give a thermal diagram, showing a single eutectic point.

Azobenzene forms the compounds $4SbCl_3,C_{12}H_{10}N_2$ and $4SbBr_3,C_{12}H_{10}N_2$.

These compounds can only be obtained by seeding the fused mixture with some of the compound which had been prepared previously.

Benzil does not combine with antimony haloids.

The order of diminishing reactivity with antimony haloids is *s*-diphenylethane, azobenzene, stilbene, benzil.

It was shown that the magnitude of the optical exaltation increases in the same order.

The effect of increasing the number and position of phenyl groups and also of carbonyl groups on the reactivity with antimony haloids was discussed, and shown to be in agreement with the exaltation of molecular refractive power.

In all cases conjugation diminishes the reactivity with antimony haloids and increases the exaltation.

Thermal analysis thus provides a useful method of tracing the conjugation of the residual affinity of the unsaturated atoms and groups CH:, N:, CO, with the phenyl groups in compounds of the type Ph . x . x . Ph.

127. "*The Absorption Spectra of Various Substances containing two, three, and four Benzene Nuclei.*" By John Edward Purvis.

The author has carried out an investigation of substances containing two, three, and four benzene nuclei united either with simple aliphatic residues or with inorganic radicles or elements, to see how far and in what directions the vibrations of the various centres influence the absorption phenomena, and particularly as regards the effect on the benzene bands. The substances examined were: *s*- and *as*-diphenylcarbamides, *s*-dibenzylcarbamide, *s*-diphenylthiocarbamide, triphenylguanidine, phenyl diphenylcarbamate, tribenzylamine, diphenyl phthalate, triphenylacetic acid, tribenzoin, triphenylphosphine, triphenyl phosphate, tri-*o*-tolyl phosphate, tri-*p*-tolyl phosphate, and tetraphenylsilicane.

128. "*Kinetics of the Decomposition of Acyl Derivatives of Phenols by means of Alcohol in Presence of Acids and Alkalis.*" (Preliminary Note). By Marian Jones and Arthur Lapworth.

The abstract of a paper by McCombie and Scarborough on "The Velocity of Saponification of the Acyl Derivatives of the Substituted Phenols" has recently appeared (vol. xxx., p. 107). The present authors have been engaged for more than a year on certain aspects of the subject, having taken up the work primarily with the object of throwing further light on the mechanism of the acid hydrolysis of esters.

Phenyl acetate has been most closely studied, special attention having been paid to the catalytic influence of acids and alkalis on the decomposition which it undergoes in alcoholic solution. With both agents the main reaction in the first instance consists in the irreversible formation of free phenol (or alkali phenoxide) and ethyl acetate, so that complete saponification is largely the result of two successive reactions, the second being saponification of ethyl acetate complicated by the formation of phenoxide.

The present authors have studied only the speed at which the first reaction takes place, by estimating the amount of phenol (or phenoxide) formed after varying periods. The influence of free phenol or phenoxide in excess has also been examined. Both acids and alkalis greatly accelerate the speed of the first reaction, and the relative influence of the two types of agent is of the same order of magnitude as in the case of the hydrolysis of alkyl esters, and there is therefore no reason to suppose that the mechanism of hydrolysis is different in phenyl and alkyl esters.

As phenyl is not detached from oxygen unless under conditions of exceptional severity, it must be concluded that hydrolysis of an ester, whether by acids or alkalis, involves the severance of the molecule at the point (1), and not at (2):

$$X{\cdot}CO\underset{(1)}{—}O\underset{(2)}{—}Alk,$$

and the analogy to amides and allied compounds is complete.

It is now fairly generally agreed that during hydrolysis and esterification by acid catalysts a complex (ionised or non-ionised) of catalyst and the two principal reacting components is formed which may decompose so as to yield carboxylic acid and alcohol or ester and water (and catalyst) on the other. The symmetry of the reactions, combined with all the data now available, suggests that the hydrogen atom in the "polymolecule" is labile, in the intramolecular sense, and may be regarded as influenced by all three oxygen atoms. The authors venture to suggest that the symbol—

$$\left[CH_3{\cdot}C\begin{matrix}\diagup(OEt)\diagdown \\ —(OH)\cdots \\ \diagdown(OH)\diagup\end{matrix}H\right]Cl,$$

which is not inconsistent with modern views on valency, is the most satisfactory one that can at present be devised for the hypothetical complex obtained during the hydrolysis of ethyl acetate by aqueous hydrochloric acid.

The work on the kinetics of the decomposition of phenyl acetate is being continued by one of the authors (M. J.), and examination is also being made of the applicability of phenyl acetate as an acetylating and dehydrating agent.

(To be continued).

FARADAY SOCIETY.

Ordinary Meeting, April 22, 1914.

Prof. Alfred W. Porter, F.R.S., in the Chair.

Mr. Charles R. Darling read a paper on "*Recording Pyrometers,*" in connection with which a full display of the most recent types of instruments was exhibited.

After referring to the pioneer work of Le Chatelier and Roberts-Austen in connection with high temperature records, the author referred to the types of pyrometer at present in use, which were capable of yielding continuous records, and dealt with the special applications of each class. The requirements of modern furnace practice in relation to records were next dealt with, a distinction being made between instruments suitable for laboratory and workshop respectively. Typical thermoelectric recorders were then described, the essential features in all cases being (1) the intermittent contact of the pointer of the indicator with the moving chart, which, in conjunction with an inking device, produced a mark indicating the temperature; (2) an arrangement consisting of an automatic switch which enabled records from several pyrometers to be secured on the same paper. The special advantages of the Siemens-Halske, Leskole, Foster, Thread, Paul, and Leeds-Northrup recorders were described by reference to the actual apparatus. It was pointed out that any of these recorders could be used in conjunction with radiation pyrometers, the chart being specially divided for such purpose. Recorders for resistance pyrometers were next described, the advantage of this type being superior sensitiveness. The examples chosen for description were the forms due to Callendar, Paul, and Northrup. It was pointed out that as in the latest patterns of recorders considerable power is available, controlled by the pyrometer, it was highly probable that the automatic control of furnace temperatures would be realised in the near future, the mechanism being utilised to regulate the supply of gas, oil, electric current, or coal-dust when continuously fed. In conclusion, a tribute was paid to the National Physical Laboratory for the excellent work performed in standardising recorders and pyrometers generally, so that all types could now be relied upon to agree in their indications.

Dr. J. A. Harker referred to the usefulness of the paper in view of the scarcity of literature on the subject, and he praised the excellence of the instruments exhibited. He hoped some information would be forthcoming with regard to the comparative life and efficacy of the various types. Some confusion in pyrometric measurements had sometimes arisen on account of the two systems of standardisation in use, namely, the usual method of comparison by reference to the melting-points of certain metals, and by reference to one fixed point, namely, the melting-point of potassium sulphate. This was often assumed, following the older workers, to be 1015° C., whereas it was actually about 1070°.

Mr. R. S. Whipple thought the difficulty of working the Callendar instrument had been overrated; over 400 of these were in use in charge of men not specially skilled.

Much work had been done with recorders in the control of heat supply. He instanced a steel works in which by the regulation of the hot-air mains a constant temperature of 700° C. was maintained to within 10°. A spectroscope used for measuring the velocities of stars in the line of sight was being kept at a temperature constant within $\frac{1}{100}$° C. He further instanced a large soldering iron used for tinplate, where constancy of temperature was most important. which was being regulated by recorder control.

Mr. C. E. FOSTER dwelt on the necessity of educating the user to want control. He emphasised the advantages of base metal thermo-couples which gave large and constant e.m.f.'s.

Mr. E. H. RAYNER hoped the author would add to his paper a table of standard melting-points so that users of pyrometers could know what temperatures for standardising were recommended.

Mr. R. W. PAUL, referring to the motor drive, for which he disclaimed originality, said that it was necessary to have ample power so as to have a large margin to waste in governing. Surprising accuracy of speed was then attainable.

Mr. DARLING replied to the discussion. The Callendar instrument was admirable where there was no vibration. He agreed as to the future of base metal couples, as homogeneous alloys could now be obtained, but above 1200° C. radiation pyrometers should be used.

Dr. E. B. R. PRIDEAUX read a paper on "*Diffusion and Membrane Potentials.*" (Will be inserted in full).

A paper by Dr. R. E. SLADE and Mr. W. G. POLACK on "*The Acidic and Colloidal Properties of Aluminium Hydroxide*" was read by Dr. Slade.

1. The conclusions of Mahin, Ingraham, and Stewart that aluminium hydroxide has no acidic properties are criticised.

2. Experiments on the conductivity of sodium aluminate solutions show that there is no evidence of the existence of colloidal aluminium hydroxide in these solutions, as was supposed by Hantzsch. Whenever hydrolysis takes place crystalline aluminium hydroxide is deposited.

3. An examination of sodium aluminate solutions in the ultra-microscope gave no definite evidence as to the existence or non-existence of colloidal particles. In the colloidal aluminium hydroxide solutions of Crum it was found that the number of amicrons present was very much greater than the number of submicrons.

Mr. A. M. WILLIAMS presented a "*Note on Negative Adsorption.*"

The paper summarised the results of experiments in which it had been found that with some electrolytes in water the "adsorption" was at first positive, increased to a maximum, decreased, passed through zero, and then became negative. Attention was therefore drawn to the fact that with different concentrations of the same solution both positive and negative "adsorption" of the solute might be observed. Hence both solvent and solute must be regarded as being adsorbed.

Mr. J. H. ANDREW communicated a paper on "*The Embrittling of Iron by Caustic Soda.*"

Small flat specimens of wrought iron, rough filed and highly polished, were immersed in a concentrated aqueous solution of caustic soda at 100° C. for periods lasting over several months. The specimens were examined from time to time, and it was found that—(1) The initial corrosion of the polished metal is less than that of the unpolished, bu eventually both become highly crystalline, the surface of the two being similar, and their corrosion rate is approximately the same.

The re-crystallisation of the specimens causes them to become extremely brittle; the brittleness eventually disappears, however, with prolonged immersion, and during the treatment with soda, hydrogen gas is evolved.

The rate of corrosion of wrought iron increases with time, attains a maximum and then decreases, the corrosion, after a very prolonged immersion in caustic soda, being extremely slight. It has been suggested that the corrosion is due to the iron being constituted of two phases, a crystalline phase and an amorphous phase, which surrounds the crystals and binds them together.

It is suggested that when a duplex metal of this nature is immersed in an aqueous solution of caustic soda, electrolysis sets in, iron going into solution at the anode, and hydrogen is liberated at the cathode, whilst sodium ferrite is formed in solution.

The hydrogen after giving up its charge at the cathode, is partially liberated and partially occluded by the metal. It is this occlusion of, and diffusion into, the interior of this hydrogen which brings about crystalline growth and brittleness in the metal, the hydrogen being first absorbed by the amorphous film existing between the crystals, thereby forcing the crystals apart. When both the amorphous and the crystalline metal have become saturated, or partially saturated, with hydrogen, the metal may be considered as constituting a hydrogen cell, the potential difference depending upon the concentration of the hydrogen in the two phases; this will be less than the potential difference between the two metallic phases, and the corrosion will diminish.

The decrease in brittleness after prolonged immersion is probably due to an equilibrium between the hydrogenised phases being established, the initial brittleness being due rather to the molecular rearrangement of the metal brought about by occlusion and evolution of hydrogen, rather than to the mere presence of hydrogen in solution. It is quite possible that the original amorphous material is destroyed, new amorphous material eventually being formed.

Experiments were carried out with the idea of showing that hydrogen actually did diminish the rate of corrosion. An electrolytic iron was heated to 1000° C. in hydrogen, and allowed to cool in the gas. The specimen after this treatment corroded extremely slowly, whereas another sample of the same material untreated corroded at the normal rate.

It may be concluded from these experiments that the passivity of iron produced by immersion in caustic soda is due to the decrease in potential difference between the crystalline and amorphous phases, produced by occlusion of hydrogen.

A 0·5 per cent carbon steel is affected to a much less degree by caustic soda solution.

The re-crystallisation of electro-deposited iron found by Stead and Carpenter to occur when the metal is allowed to slowly cool through the A_{r3} critical point, is explained upon the basis of hydrogen evolution; as the iron cools through the critical point the evolution of hydrogen effects a re-crystallisation of the metal.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clviii., No. 14, April 6, 1914.

Use of Manganous Oxide for the Catalysis of Acids. Preparation of Pentamethylenic Aldehydes and Acetones. Formation of Cyclopentylamines.—Paul Sabatier and A. Mailhe.—Manganous oxide, obtained from manganous carbonate, can be used as catalyst in the formic reduction of acids at a temperature between 300° and 360°. The acid to be reduced is introduced into the catalysis tube with double the volume of formic acid. The portions of this latter acid, which are not used in the reduction, are totally converted into gaseous products. In the condensed product the water formed is eliminated and the aldehyde is separated from unchanged acid by fractionation. Cyclopentanone, C_5H_8O, can be obtained by the decomposition over manganous oxide at 350° of adipic acid. β-Methylcyclopentanone can be prepared similarly, and both substances readily yield oximes, from which cyclopentylamines and β-methylcyclopentylamines can be obtained by direct hydrogenation over nickel.

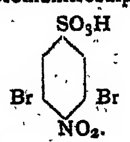
Nitride of Iron.—G. Charpy and S. Bonnerot.—When metallurgical ferrous products are exposed to the action of ammonia iron nitride of formula Fe_2N is formed. If very fine shavings of the metal are used it is quite easy to transform them completely into nitride. The nitride is reduced to ammonia by means of hydrogen at 350°. The velocity of the reaction increases rapidly as the temperature is raised and becomes very great at 500° to 600°. When the nitride is heated in nitrogen at atmospheric pressure decomposition does not begin till a temperature of 550° is reached. It is probable that the small quantities of nitrogen which are found in cast-irons and steels are present in the occluded state, or in a state of combination with an element other than iron.

Atomic Weight of Nebulium and Temperature of Nebula of Orion.—H. Bourget, Ch. Fabry, and H. Buisson.—The very marked double line 3726—3729 in the ultra-violet is not attributable to any known gas. By the calculation of the limiting order of interference, which is a function of the atomic weight and the absolute temperature, it is found that the atomic weight of the unknown gas, nebulium, is about 3. The maximum temperature of the luminous gas is about 15000°. A strong green ray ($\lambda = 5006$) is also due to an unknown gas. It is emitted by a gas of atomic weight greater than that of hydrogen but less than that of the gas which emits the ultra-violet ray. It is noteworthy that, according to Rydberg's recent classification of the elements, there are two unknown elements between hydrogen and helium having atomic weights 2 and 3 respectively.

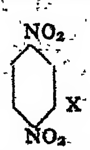
Quantitative Study of the Absorption of Ultra-violet Rays by Diketones of the Fatty Series.—Jean Bielecki and Victor Henri.—The absorption of acetone increases a little in alkaline and diminishes in acid solution. The presence of two carbonyls in the conjugate position produces an absorption band which is displaced 150—200 U.A. towards the red with reference to the characteristic band of a single carbonyl. Thus there is a hypsochromic effect. The presence of two separated carbonyls in the γ-position produces an augmentation of the characteristic band but no displacement; there is thus only a hyperchromic effect. The β-diketones show a spectrum which varies greatly according to the reaction of the medium and the nature of the solvent.

Atti della Reale Accademia dei Lincei.
Vol. xxiii. [i.], No. 5, 1914.

Nitrosubstituted Benzenes obtained from Corresponding Amino Derivatives.—G. Körner.—With many substituted anilines the substitution of an amide group by a nitro group is easily performed, and the yield is good. In other cases the reaction does not take place, or else the amount of substituted product obtained is negligible. An aqueous solution of dibromosulphanilic acid when treated with nitrous acid and an excess of sodium nitrite in aqueous solution gives the dibromonitrosulphonic acid—



In the same way the dinitrobenzene monohalogen derivatives of the type—



can be obtained, starting from the corresponding nitroaniline. The author has prepared the 1.4.5-dinitrochloro, bromo, and iodo benzenes, and investigated their properties.

Researches in Systematic Chemistry: Ruthenium, Rhodium, Palladium.—G. A. Barbieri.—Trivalent ruthenium gives with acetyl acetone a crystalline red compound, monomolecular in bromoform, and soluble in the solid state in aluminium acetyl acetonate. With molybdic acid rhodium forms complex compounds, rhodimolybdates, which both chemically and crystallographically are completely analogous to the corresponding complex molybdates of aluminium, Fe^{III}, Cr^{III}, and Co^{III}. Divalent palladium gives an acetyl acetonate which is monomolecular in bromoform, and which forms mixed crystals with cupric acetyl acetonate.

MISCELLANEOUS.

Royal Institution.—On Tuesday next, June 2, at 3 o'clock, Prof. A. Fowler will begin a course of two lectures at the Royal Institution on "Celestial Spectroscopy"; on Thursday, June 4, Prof. Silvanus P. Thompson will deliver the first of two lectures on "Faraday and the Foundations of Electrical Engineering"; and on Saturday, June 6, Mr. S. Goetze will commence a course of two lectures on "Studies on Expression in Art." The Friday Evening Discourse on June 5 will be delivered by Prof. W. H. Bragg on "X Rays and Crystalline Structure," and on June 12 by His Excellency the Hon. Walter Hines Page (the American Ambassador) on "Some Aspects of the American Democracy."

Australasian Medical Directory.—Messrs. Butterworth and Co. (Australia), Ltd., 4, Bell Yard, Temple Bar, London, have just published "The Medical Directory (incorporating "Loxton's Medical Directory") of Australia, Tasmania, New Zealand, Pacific Islands, Malay States, China, Japan, Hong Kong, &c.," by F. W. Loxton. Amongst the contents may be mentioned—Appointments in Hospitals, List of Doctors in Australasia, Commonwealth Census, Climates of Australasia, Particulars of Hospitals, Medical Boards in New South Wales, Queensland, Victoria, South Australia, and Western Australia, Registration in the Various States, New Zealand Medical Acts, List of Public Hospitals, &c. The volume also contains a section dealing with the Laws Relating to Medical Practitioners in the various states; Mr. Baxter Bruce, of the New South Wales Bar, is responsible for this section.

MEETINGS FOR THE WEEK.

Tuesday, 2nd.—Royal Institution, 3. "Celestial Spectroscopy," by Prof. A. Fowler, F.R.S.

Wednesday, 3rd.—Society of Public Analysts, 8. "The Insoluble Bromide Value of Oils and its Determination," by Alexander Gemmell. "Determination of Iridium in Platinum-Iridium Alloys," by C. O. Bannister. "Symbolical Representation of Analytical Operations" and "Properties of some Chlorhydrocarbons and their Uses in Chemical Analysis," by L. Gowing-Scopes. "Changes in the Character of Fats during the Process of Cooking," by Helen Masters and H. L. Smith. "Chief Source of the Loss of Sulphuric Anhydride and of Chlorine by Ashing Substances containing these Constituents," by J. O'Sullivan.

Thursday, 4th.—Royal Institution, 3. "Faraday and the Foundations of Electrical Engineering," by Prof. Silvanus P. Thompson, F.R.S.

— Chemical, 8.30. "Studies in the Succinic Acid Series—Part I., The Chlorides of Succinic and Methylsuccinic Acids and their Constitution," by G. F. Morrell. "Dilution Limits of Inflammability of Gaseous Mixtures—Part I, Determination of Dilution Limits; Part II., The Lower Limits in Air of Hydrogen, Methane, and Carbon Monoxide," by H. F. Coward and F. Brinsley. "Comparative Study of the Absorption Spectra of some Compounds of Phosphorus, Arsenic, Antimony, and Bismuth," by C. R. Crymble. "Reactions of β-Hydroxy-α-amino-compounds as Cyclic Structures," by J. C. Irvine and A. W. Fyfe.

Friday, 5th.—Royal Institution, 9. "X-rays and Crystalline Structure," by Prof. W. H. Bragg, F.R.S.

Saturday, 6th.—Royal Institution, 3. "Studies on Expression in Art," by Sigismund Goetze.

THE CHEMICAL NEWS.

Vol. CIX., No. 2845.

THE PREPARATION OF EYE-PRESERVING GLASS FOR SPECTACLES.*

By Sir WILLIAM CROOKES, O.M., F.R.S.

Since March, 1909—in connection with the Glass Workers' Cataract Committee of the Royal Society—I have been experimenting on the effect of adding various metallic oxides to the constituents of glass in order to cut off the invisible rays at the ultra-violet and the infra-red ends of the spectrum. The work has been done chiefly in my own Laboratory. I have been aided by Mr. Harry Powell, of the Whitefriars Glass Works, who prepared several pots of coloured glass from my formulæ on a much larger scale than could be made outside a Glass works. From these glasses cylinders and sheets were made.

The main object of this research is to prepare a glass which will cut off those rays from highly heated molten glass which damage the eyes of workmen, without obscuring too much light or materially affecting the colours of objects seen through the glass when fashioned into spectacles, but the work necessitated an examination of the screening properties of glass plates for ultra-violet and luminous light, and therefore the research was enlarged so as to embrace the three forms of radiation.

Radiation from Molten Glass.

In order to ascertain what rays are given off from molten glass I spent some time at the Glass Bottle Works of Messrs. Nuttall and Co., St. Helens, and took many photographs of the spectra of the radiations.

Photo-spectrographic and other examinations were made of the radiation emitted from the molten glass under working conditions. Full details of the experiments and results are given in this paper.

At the time I visited Messrs. Nuttall's Works light green bottle-glass was being made; the mixture is composed of silica, sodium sulphate, and calcium carbonate or sulphate. The materials are melted in a large fire-brick tank, heated by a flaming mixture of gas and air playing on the surface. The gas is made some distance from the furnace in a "producer." Gas and air are conducted by separate channels to the upper part of the tank, where they mix and burn, the flame reverberating from the arched roof and heating the glass mixture to the requisite degree.

The area of the tank of molten glass is about 82 square yards, and it contains from 300 to 350 tons of the mixture. There are several such tanks in the works. The tank is divided by a fire-clay partition into two unequal parts. At the lower part is an opening through which the melted glass can flow. The larger portion of the tank, where the materials are melted together at a high heat, has a surface of about 63 square yards. This is called the "melting end"; when the mixture is well fused and homogeneous the molten glass flows through the opening into the "working end" of about 19 square yards, where the heat is less and the glass is in a viscous state. Fire-clay rings of 18 inches internal diameter and a foot deep float on the surface of the viscid glass; any scum on the surface of the tank is thereby kept from contaminating the surface of the glass inside the ring. One ring floats opposite each working opening, and the workmen withdraw the requisite quantity of glass for each operation from the inner surface of the ring.

* Read before the Royal Society, November 13, 1913. From the *Philosophical Transactions of the Royal Society*, Series A, vol. ccxiv., pp. 1—25.

The light from the melting end of the tank, viewed through a working opening, was brilliant white with a tinge of orange; it was with difficulty the unprotected eye could make out any details. Viewed through dark glasses the surface of the metal in the tank appeared as a seething mass in constant commotion. The surface in the working end was more easy to see. It was of a bright yellow incandescence, and comparatively quiet.

It is not certain what the temperatures are at each end of the tank. So far as one could judge the temperature at the melting end is about 1500° C., and at the working end decidedly less - say, 1200°.

About each opening, especially at the melting end, thin white vapours rose and settled on the surrounding cooler parts. A piece of paper held in this vapour instantly ignited. Examined with a hand spectroscope the yellow line of sodium was seen to be brilliant in this vapour, but the light from the molten glass showed a continuous spectrum in which the sodium line was visible. On one or two occasions a black line was seen in place of the yellow sodium line, showing a reversal. Some of the condensed vapour was collected from the cool sides of the working opening and chemically examined. It was found to consist principally of sodium and calcium sulphates, with a little sodium chloride.

Photo- and Thermo-graphic Experiments.

The spectrograph used for taking photographs of the radiation from the molten glass is the one I described in *Roy. Soc. Proc.*, vol. lxv., p. 237, May, 1899. It has two quartz prisms, each made up of two halves, one half being right- and the other half left-handed, according to Cornu's plan for neutralising the effect of double refraction. The collimating and camera lenses and the double condensers are also of quartz cut in the same fashion. The slit jaws are made of two acute angled quartz wedges, edge to edge. The refracting prisms are of 60° angle, and each face is 35 mm. by 42 mm. The lenses are 52 mm. diameter and 350 mm. focus. The condensers are plano-cylindrical, one being double the focus of the other. In order to ascertain the exact position of any part of the spectrum I might obtain from the radiation from the molten glass, I took photographs on each plate of an alloy of equal molecular weights of zinc, cadmium, tin, and mercury. This alloy gives throughout the photographic region lines, the wavelengths of which are well known.

The instrument sloped downwards, so as to allow the radiation from the surface of the melted glass to enter the condensers, prisms, and slit along the axis. To prevent the great heat injuring the spectrograph Mr. Nuttall allowed the opening to be bricked up, leaving a hole a few inches square in the middle. This was covered with an iron plate with a 2-inch hole in it, and over this a quartz plate was fixed.

Panchromatic films were used. These are sensitive beyond λ 7800 in the ultra-red, and to the highest ultra-violet rays which will pass through quartz (about λ 2100). Flexible films had to be used in preference to glass, as they had to follow the curvature of the focal plane. Many preliminary experiments were made to ascertain the extent of spectrum to be recorded, its best position on the films, and the exposures needed. The slit of the instrument was generally placed about 4 feet from the molten surface, and it was found that from ten to fifteen minutes were required to produce a faint image on development. On each film, immediately before the radiation picture was taken, a photograph of the spark spectrum of the quadruple alloy was impressed on the film, in such a position that the two spectra would overlap to a very slight degree.

No. 1 photograph was taken at the working end of the tank, where the temperature was lower than at the other end. An exposure of twenty minutes was given, the width of slit being 0·025 mm.

No. 2 photograph was taken in the same conditions as No. 1, but with an exposure of forty-five minutes.

No. 3 photograph was taken at the melting end, where

the heat was fiercest. The width of the slit was reduced to 0·1 mm., and an exposure of half-an-hour was given.

No. 4 photograph, at the melting end, was exposed for one hour.

No. 5 photograph, at the melting end, was exposed for two hours.

No. 6 photograph, also at the melting end, was exposed for three hours.

It was not found practicable to give longer exposures.

Whilst these experiments were in progress, other experiments at another opening at the hottest end were tried to see if X-rays could be detected. Sensitive films were wrapped in black paper and then in lead foil in which designs had been cut. These were exposed for varying lengths of time, as near as it was safe to put them to the radiation from the molten glass, bearing in mind that the heat might affect the films. On development, no image of the stencil designs on any of the films could be detected. These results confirm those previously obtained by Dr. Burch—that X-rays are not emitted by the highly incandescent molten glass.

A careful examination of the six photographs shows a general progressive character, the extent of spectrum photographed extending into the ultra-violet as the length of exposure increases.

The extent of spectrum into the region of the ultra-violet is conveniently shown in the following tabular form*:—

No. 1 photograph, exposed twenty minutes, extends to λ 4520.

No. 2 photograph, exposed forty-five minutes, extends to λ 4320.

No. 3 photograph, exposed thirty minutes, extends to λ 3790.

No. 4 photograph, exposed sixty minutes, extends to λ 3640.

No. 5 photograph, exposed 120 minutes, extends to λ 3595.

No. 6 photograph, exposed 180 minutes, extends to λ 3345.

Taking the ordinary limit of visibility to lie between λ 3900 and λ 7600, it is seen that with an exposure of three hours to the highest heats the strength of impression does not extend much into the ultra-violet. The heat rays are very strong, and if injury to the eye is caused by exposure to radiation from the molten glass, a protective glass should be opaque to the infra-red rays.

These being present in the radiation from molten glass in far greater abundance than the ultra-violet rays, the inference is that it is to the heat rays rather than to the ultra-violet rays that glass workers' cataract is to be ascribed. It is, however, certain that exposure to excess of ultra-violet light also injuriously affects the eye.

That the ultra-violet rays act on the deeper-seated portions of the eye is shown by the intense fluorescence of the crystalline lens induced by these rays.

Besides the invisible rays at each end of the spectrum, the purely luminous rays, if present in abnormal intensity, are found to damage the eye. It therefore would be an advantage if in addition the obscuring glass for the spectacles were to be of a neutral or grey tint.

Synthetic Preparation of Glasses.

It soon became evident that my best, if not only, chance of solving the problem was to make different glasses in my own Laboratory, with the addition of known quantities of pure metallic oxides and earths as colouring or absorbing materials. Lapidary apparatus for cutting, grinding, and polishing was also necessary so that the synthetically made glasses could be cut into plates—polished so as to be tested photographically in the spectrograph already described—and also tested for the percentage of heat rays they obstructed.

Many preliminary experiments were made on the preparation of a clear and colourless glass or flux to serve as a basis for the colouring with the various metallic oxides. Finally, two kinds of soda glass not containing lead were chosen, and Mr. H. Powell, of the Whitefriars Glass Works, who had assisted me in the preliminary trials by supplying me with many kinds of glass of different composition and fusibility, made a quantity of these fluxes and supplied them in a crushed condition.

In my earlier laboratory experiments the mixture of colouring matter and granulated flux was put into a small "gold pot" of Morgan's Crucible Co., and gradually heated over a "Meker" gas burner. It is advisable to have one at least of the colouring constituents in the form of nitrate so that its decomposition by heat shall mix and stir the constituents. The decomposition of the nitrate causes a little frothing; therefore it is necessary to add the mixture gradually to the crucible, to avoid frothing over. When all is added and the contents well fritted, the hot crucible is removed to an electric furnace and the temperature slowly raised until the glass is quite fluid. It is stirred at frequent intervals with a stout platinum rod. After an hour the stirring is discontinued, and the temperature kept up for an hour and a-half. The current is then cut off, the openings in the furnace plugged with asbestos to prevent draughts, and the whole allowed slowly to cool to anneal the glass. In some cases the composition of the glass was such that the melting-point had to be raised above 1400° C., and as this temperature was beyond the safe limit with the platinum strip furnace, a blast-furnace fitted with a "Lennox" electric blower was used; with this arrangement larger quantities of glass could be raised with safety to a much higher temperature.

There are two conditions I have endeavoured to secure of the finished glass—each of great importance. One, the most essential, is the absence of all streaks, striæ, and irregularities of density; the other, the absence of air bubbles. The first is obtained by repeated stirring and perfect admixture; the freedom from air-bubbles is secured by leaving the glass in perfect repose while the heat is at the highest point. On these and other points I have been much aided by reading an early paper by Faraday "On the Manufacture of Glass for Optical Purposes," the Bakerian Lecture read before the Royal Society in 1829 (*Phil. Trans. Roy. Soc.*, 1830, p. 1). On a small scale it is almost impossible to avoid slight striæ owing to differences of density caused by the long continued heat volatilising some of the soda. Faraday was much harassed by this dilemma in the manufacture of his optical glass, and tried many experiments to ascertain the cause. To get rid of air-bubbles Faraday used spongy platinum in powder sprinkled over or added to the bulk of the melted glass. This was found to act pretty well, making the bubbles rise in the same manner as a piece of bread causes bubbles to rise when thrown into a glass of effervescing liquid. To get the full benefit from this device, however, the glass must be kept perfectly quiet and at the highest temperature for a longer time than in my case was always practicable.

When the crucible has cooled slowly for about twelve hours it is removed from the furnace, and the solid cone of glass removed by breaking the crucible by a few judicious blows with a light hammer. The lump of glass is now taken to the lapidary's table, and slit across the middle and a plate cut from it, which is ground and polished to a determined thickness, usually 2 millimetres.

Testing Synthetic Glasses for Opacity to Ultra-violet Light.

The plates are now tested for the opacity of the glass to the rays of the ultra-violet end of the spectrum. The

* In connection with this table the following scale for correlating colours with wave-lengths will be useful:—

Wave-lengths 7230 and below = Infra-red.

	λ		λ			λ		λ	
From	7320	to	6170	= Red.	From	5920	to	4550	= Blue.
,,	6470	,,	5850	= Orange.	,,	4550	,,	4240	= Indigo.
,,	5850	,,	5750	= Yellow.	,,	4240	,,	3970	= Violet.
,,	5750	,,	4920	= Green.	,,	3970	and above		= Ultra-violet

spectrograph with complete quartz train, already referred to, was used. By superposing on the radiation from a Nernst lamp the light from a high-tension electric discharge between poles of pure metallic uranium it is possible to produce a practically continuous beam extending from λ 2000 to λ 8000, and the absorption of such a beam of radiation, produced by flat plates 2 mm. thick of all my experimental glasses, has been thereby recorded.

To ascertain the amount of heat obstructed by the plates of glass I first used a Melloni's thermo-pile as described in his papers,* but I soon found that modification was needed as the pile responds to the orange and red rays as well as to the infra-red.

Plates of dark smoky quartz 2 mm. thick were tested with the thermopile, and it was found that they transmitted nearly all the heat whilst cutting off 80 or 90 per cent of the light. Biotite (black mica) exerts a similar effect, and is more easily experimented with than smoky quartz. For many years I have used biotite for cutting off light and transmitting heat; I accordingly investigated the properties of many specimens of black and dark brown mica to find out which would be best for this special purpose.

Selection of Black Mica (Biotite) for Diathermancy.

Samples of dark brown and black mica vary considerably in their power of obstructing light and transmitting the infra red rays. By the kindness of friends connected with the mining and importation of mica I have been able to examine a large number of samples from different parts of the world.

Some very fine pieces of black biotite were sent by Messrs. Attwater and Sons, who tell me they were mined by them in the extreme north of Norway from a cleft in a mountain at about 2000 feet. This mica is extremely regular in the thickness of the flakes which can be split from it, and the colour of thin pieces is uniform. A piece 0·07 millimetre thick entirely cuts off the luminous rays, and even the sun's disc is only just seen through a flake 0·06 millimetre thick.

In addition to specimens from Norway, Messrs. Attwater and Sons sent me black biotite from German South-East Africa, and some fine pieces of "black amber" mica from Africa. The African mica is uniform in colour, and easily splits into flakes of great regularity. The German mica is difficult to split into uniformly regular flakes, and therefore varies considerably in colour.

Messrs. F. Wiggins and Sons allowed me to select some large sheets of dark brown and black biotite from their stock. The sheets when split are uniform in colour, and in thicknesses below about 0·30 mm. are sufficiently transparent to allow the eye to detect a Nernst glower. Mica differs, however, in transparency, one flake from a sheet being opaque at 0·24 mm., while a flake from another part of the same sheet is slightly transparent in a thickness of 0·34 mm. I also received good black mica from Mr. Henson, who gave as its locality Renfrew, Canada.

Many experiments have been carried on with all these kinds of brown mica to find a quality which would cut off the rays which at Kew were called the "scorching rays" (the infra-red rays), and some of the best results were obtained with the Norwegian mica from Messrs. Attwater and Sons, and the Black Amber African mica from Messrs. Wiggins and Sons.

There is a certain gradation of transmitted rays according to the thickness of the dark brown micas. All of them cut off rays at the blue end of the spectrum, and as the thickness increases the portion of the spectrum obstructed rapidly tends towards the red end, until a mica is found which affects the photographic plate in a narrowed band round the line B, the exposure being from ten to twenty times as long as would be required for this part of the spectrum to impress itself, were no mica to intervene. To increase the thickness of the dark mica soon obstructs all rays in the red visible to the eye.

Examined by the thermometric apparatus, a thermopile, and in the radiometer balance—described below—the dark micas which allow any trace of visible rays to pass are strongly diathermic. As the thickness of mica increases the deflection of the index spot of light gets less and less, until there is very little action at all. Judging from analogy it is most probable that as the thickness increases the heat rays are cut off in regular gradation from the line B in the red to the longest rays of heat which will affect the radiometer balance.

This is only a hypothesis and does not take into account the possibility of their being dark bands in the infra-red portion of the heat spectrum. Still the hypothesis as a working tool has been of considerable use, and has helped me to select dark mica obscuring media—giving good and concordant results.

Were I to take at random a piece of black mica which would cut off all the rays visible to the eye, and not allow any red and ultra-red rays to pass that would affect the pan-chromatic plate, I should have no certainty that the piece of mica would not cut off some of the heat rays which the glass transmitted. If, on the other hand, I select a piece that allows the red rays near the lines B and C to pass (as shown on the photo-spectrograph), some of the action on the radiometer balance would be due to the luminous red rays, and it is not advisable to entirely cut these off as the residual colour thereby might be affected. The plan ultimately adopted was gradually to increase the thickness of the mica until the photo-spectrograph showed that the visible red had just ceased to affect the plate. After experimenting on some hundred kinds and thicknesses of brown and black mica I succeeded in getting a piece which appeared to satisfy all requirements; the examination of the different kinds of glass made in my laboratory during the last four years has been carried on by help of this specimen.

(To be continued).

FACTORS INVOLVED IN OPENING UP THE FIELD OF UNUSED ELEMENTS.

By CHAS. BASKERVILLE, Ph.D., F.C.S.
Professor of Chemistry and Director of the Laboratory, College of the City of New York.

In attempting to classify the accepted elements so that one group, or pseudo-group, contains those elements designated "unused" or "little used," one is confronted with many difficulties. The prime difficulties involve the purpose of the classification and the extent of the use. What concerns us this evening is admittedly of technical significance, and must involve economic considerations, yet may not be devoid of abstract scientific interest.

Are we to confine our discussion to the elements or their compounds, or are we to include both? I give herewith a table of "unused" or "little used" elements, whose compounds are used more or less. The periodic classification is followed for convenience. This and two other tables which are given later are confessedly imperfect and based upon capricious opinion, but perhaps may serve our purpose.

Elements Little Used or not Used, but whose Compounds are used More or Less.

0.	1.	2.	3.	4.	5.	6.	7.	8.	Unclas.
	Li	Mg	B	S	As		F	Co	
	K	Ca		Zr			Br		
		Ba		Ce			I		
		Ra		Th					

* "On the Free Transmission of Radiant Heat through Different Solid and Liquid Bodies" (*Ann. de Chim. et de Phys.*, vol. liii., p. 1); Taylor's "Scientific Memoirs" (vol. i., p. 1). "New Researches Relative to the Immediate Transmission of Radiant Heat through Different Solid and Liquid Bodies" (*Ann. de Chim. et de Phys.*, vol. lv., p. 337); Taylor's "Scientific Memoirs" (vol. i., p. 39).

Over one-third of the accepted chemical elements have no serious commercial uses at present as elements or compounds. These are given in the following table:—

Elements or Compounds Unused or Little Used.

0.	1.	2.	3.	4.	5.	6.	7.	8.	Unclas.
He	Rb	Be	Sc	Ge	Cb	Se		Ru	Pr
Ne	Cs	Sr	Y		Yb	Te		Rh	Nd
A			La					Os	Sm
Kr			Ga						Eu
Xe			In						Gd
Nt			Er						Dy
			Tl						Tm
									Lu
									Tb

About one-half of these have been discovered within the last thirty years. Those so recently made known are usually classified under the two groups of "rare gases" and "rare earths." Of the latter it may be well to point out that the group is further conveniently subdivided under the heading of "rare earths" as follows":—

Rare Earths.

Ce group.		Tb group.		Yt group.	
Element.	Atomic wt.	Element.	Atomic wt.	Element.	Atomic wt.
Sc	44·1	Eu	152·0	Dy	162·5
Yt	89·0	Gd	157·3	Ho	?
La	139·0	Tb	159·2	Er	167·4
Ce	140·25			Th	168·5
Pr	140·6			Yb	172·0
Nd	144·3			Lu	174·0
Sm	150·4				

Your attention is directed to the melting-points and specific gravities of four of them.

Melting-points.

Ce = 623° C.
La = 810° C.
Nd = 840° C.
Pr = 940° C.
Al = 660° C. } Give a rough standard
Ag = 960° C. } of comparison.

Specific Gravities.

La = 6·15
Pr = 6·48
Nd = 6·96
Ce = 7·04

Cerium has about the same density as Sn (7·3), but all of them readily oxidise on exposure to air. Cerium is between lead and tin in its physical appearance, and harder than tin, while lanthanum acts much like metallic calcium, its oxide combining readily with water to form the hydroxide, being even air-slaked (combining with carbon dioxide) as does lime. I exhibit here small samples of these metals prepared in my laboratory. In passing I may state that the price of metallic cerium in Germany within a few years has fallen from 250 to 20 marks per kilo.

The word "rare" as applied above—as is the case with so many words of qualification—has changed its meaning in the light of very recent investigations, although the "rare gases" are found in the atmosphere in the following proportions:—

Noble Gases.

Name.	Atomic weight.	1 part by volume in air.
Helium..	4·0	2,450 vols.
Neon	20·0	808 „
Argon	39·9	105 „
Krypton	81·8	746,000 „
Xenon	128·0	4,846,000 „

Some of the elements mentioned above are by no means so uncommon now, and may be had in commercial quantities. I give herewith a table containing these and some other elements, many of which have been known for a long time, not now used extensively, but inviting application:—

Elements Now Available, or Easily Rendered Available, in Commercial Quantities but Little Used.

0.	1.	2.	3.	4.	5.	6.	7.	8.	Unclas.
A	K	Ca	B	Si	As	Se	Br	Co	
		Sr	Y	Zr	Cb	Te	I	Pd	
		Ba	La	Ce	Ta				
		Cd		Th					

Now that we have seen the field, let us see what are some of the factors involved in bringing it under cultivation. I know how hard the work is. I have been a field hand, for as my old friend President McIver once said, "I've ploughed new ground with a blind mule."

In some cases we lay the lack of use of the elements at once to the scarcity of known occurrences. Haber has shown that osmium is the best catalyser for making ammonia from its elements, but von Welsbach, who devised the osmium filament lamp, has calculated that there are only a few hundred pounds of osmium available in the periphery of our globe. When, however, we remember that carbon is but 0·21 per cent, while silicon is 25·3 per cent of the crust of our earth for a depth of ten miles, including the waters on the earth and its surrounding atmosphere, according to Clarke's calculations, we know that our present utilisation of the elements commercially bears but little relation to their total quantity. With some striking exceptions, man has found more or less ample sources of the elements or their compounds when it has been shown that our civilisation required them. I need but mention tungsten, thorium, vanadium, and radium in illustration. It is not the small percentage in which these elements occur, for palladium exists in nickeliferous pyrrhotites in quantities too small to be detected by even refined chemical analysis, but it accumulates in the slimes of nickel refineries, and is thus obtained in some quantity. The price fixed by possession is the deterrent in the development of the use of palladium, a fact of no individual immorality, perhaps even praiseworthy, but contrary to the law of economics. Some ten years ago one large corporation possessing a store of palladium was approached by some technologists, supported by good repute, with the idea of working out uses for that by-product. The owners said they were not interested in spending a thousand dollars on the investigation—they did not mind spending the money, but they would not be a party to lowering the price of the material in their possession, the inevitable result of extending its use. This principle is well illustrated in the history of metallic aluminium and thorium oxide, whose market quotations have fallen to one one-hundredth and two one-hundredths respectively what they were one generation ago.

On account of its great resistance to atmospheric oxidation and moisture and to the effect of sulphuretted gases, palladium has been employed for the inner mechanism of chronometers and watches, for the construction of fine balance beams, for the divided scales of delicate apparatus, for surgical instruments. It has been used for coating silver goods, and for electroplating searchlight mirrors, for soldering platinum, and in dental preparations. Palladinised asbestos, palladium sponge, and palladium black are most efficient catalytic substances for reducing purposes. This well-known fact may be flashed from the housetops without any fear of coagulating the clouds of litigation hovering over the oil-hardening situation in this country, as the parties referred to still own the palladium.

Some of these "unused" elements will be used, if the prices are made more reasonable. A very important factor in reducing the market prices of these substances is an improvement in methods of extraction. This I may illustrate from the group of rare earths, not that I mean to lead you into that maze, but because it shows how modern tools have served the purpose and gives suggestions for

needed extension with other elements in that class of "meta-elements," as Crookes termed them.

Monazite sand is essentially a phosphate of the rare earths containing variable amounts of thorium, usually 4—6 per cent. The problem of obtaining thorium compounds from that source—315,000,000 Welsbach mantles was the world's output in 1913—depends upon (1) solution, usually by baking, with concentrated sulphuric acid and leaching. Very fine grinding of the sand was essential. (2) The rare earths and thorium are then thrown out as oxalates to remove the last trace of phosphoric acid. (3) The mixed oxalates were brought into solution with the destruction of the oxalic acid, and the thorium precipitated or the oxalates were treated with ammonium oxalate, whereby the nonahydrated thorium tetra-ammonium oxalate went into solution. This thorium salt was subsequently converted into nitrate. Withal the price of thorium salts steadily declined until it seemed to reach a limit.

Muthmann and Weiss conceived the plan of distilling off the phosphorus and converting the metallic elements present into carbides. The resultant mass is hard, and is very expensive to grind in order subsequently to dissolve it. The writer later produced calcium carbide within the mixture of other carbides, using the unground monazite sand. This mass when thrown into water crumbles at once to a powder from which the suspended milk of lime is readily washed. The residual mass of carbides goes into solution in commercial hydrochloric acid from which the thorium may be precipitated at once in a form readily soluble in nitric acid. The cerium may be thrown out of the solution from the thorium precipitates, and tons of oxalic acid are now destroyed or locked up in the by-product of rare earths which are accumulating awaiting the development of uses.

Muthmann and Weiss and Hirsch in this country have applied the Hall process for the isolation of metallic cerium, whose use is now practically limited to pyrophoric alloys.

Very recently it has been proven to be distinctly profitable, according to separate patents of Soddy and Hahn, to separate meso-thorium compounds in the process of extracting and purifying the thoria. Meso-thorium rivals radium in some of its applications in radio-surgery.

The three instances cited above are given for another reason. The ideas were worked out by three college professors. Labourers must be provided for clearing the field, whether the toil be that of working out new processes to so reduce the cost of a material as to admit of its application or to develope uses not known for by-products now quoted at fictitious prices, but which do not appear at such supposititious values in the annual financial statement.

Undoubtedly the best way to work out problems of the utilisation of "undeveloped elements" is to attack them in such well-equipped and splendidly manned research laboratories as are maintained by the General Electric Co., the General Chemical Co., the Eastman Kodak Co., and others, but their up-keep involves large expenditures. Many college and university professors would welcome a subsidy for work of this character, which should be scientific, dignified, and help keep the wolf from the door. I commend for your amusing perusal "The Confessions of a College Professor's Wife" in a recent number of the *Saturday Evening Post*. I do not mean that the college professor is prepared to or should go into the factory, but he can work at an idea which should later be developed, if it has merit, on a commercial scale by the technical chemist or chemical engineer. Elaboration of this proposition, which is not novel with the speaker, is not necessary here. Suffice it to say that one so selected would bring to the problem a degree of ignorance that might be stimulating and a freedom from tradition which would admit of a display of imagination necessary to utilise material which is commercially abundant and inviting investigation.

H. B. Baker has said somewhere:—"Nothing can be of more value to science than the exhaustive study of one particular action." Weiss and Neumann have found that compressed zirconium is a conductor, whereas previous statements have been that it was non-conducting. There is need of reviewing many such statements that are handed down in the literature. Aluminium is sonorous according to so many text-books. I have a sample of very pure aluminium, a part of which was used by the late Prof. Mallet in the determination of its atomic weight, and, as he assured me, it is not sonorous. If aluminium is sonorous it is not pure. Although I have been informed that this statement is not true, if the aluminium has been rolled.

Stewart, in his charming book on "Recent Advances in Physical and Inorganic Chemistry," in referring to 1887 and the following years of feverish activity in physico-chemical research, led by Arrhenius, van 't Hoff, and the elder Ostwald, says:—"To some extent this wave appears to have spent its force. At the present day physical chemistry, except in the hands of a few exceptional researchers, has degenerated into a means of attacking the problems of pure chemistry instead of opening up new fields; and consequently there is a certain tendency to decry the subject as a mere means to an end, and not a living branch of science. This is perhaps an exaggerated view; but it cannot be denied that physical chemists of the present day are not animated by the high hopes which seem to have inspired Ostwald and others in the earlier days of the subject." Bancroft acknowledges that there is some truth in this criticism, but asserts:—"The difficulty is that most people are still struggling under the limitations imposed deliberately and consciously by Ostwald. Once these are broken through, nobody will have any cause to complain of the wave having spent its force." Stewart further says:—"It is an extremely fortunate coincidence that as the first movement declined, a second and perhaps more powerful one had succeeded it. This second movement rose with even greater rapidity than pure physical chemistry, and yet at the present day we appear to have touched only the fringe of the subject of radio-activity; so that we may look forward to a long career of fruitful investigation still before us in this department of chemistry.

The problems of sub-atomic or electronic universe have presented themselves, and at once we begin applying these new ideas to utilitarian purposes. The cryogenic laboratories have accumulated fractions from tons of liquefied air. Collie found that neon thus had incidentally luminesces under the influence of the Hertzian waves. A tube of neon serves as a detector of the nodes and loops, glowing brilliantly under the influence of the latter as if it were excited by an induction coil. Tubes of neon, prepared by Claude in Paris, electrically excited, offer a most pleasing and perhaps later on may supply an economical form of artificial light approaching sunlight.

Quantities of argon are now available from liquefied air. There are indications that, on account of its inertness, we may shortly see tungsten incandescent lamps, as Whitney puts it, with "the vacuum jar full of argon" instead of nitrogen. Troost and Ouvrard have stated that they have succeeded in causing argon to combine with magnesium vapour. Neither Rayleigh, Ramsay, nor Moissan were able to secure any evidence of the formation of compounds of argon, however. Many reactions unobserved on the laboratory scale are found to occur when dealing with large quantities of substances through long periods of time. If this were not true we should have even greater difficulty in accounting for the occurrence of such inert gases as helium in malacone, clevite, and thorianite. If it is thus barely possible that in time we shall find compounds of argon produced in the large scale operations of burning the nitrogen of the air, as carried on so successfully in Norway at present. A use of compounds of argon may then be found.

The development of radio-activity has projected us into an undreamed of realm of thought and new interests. The phenomena of radiology are closely allied to those of radio-activity. The use of Röntgen rays in medicine has

been attendant with not a few difficulties. Among them the so-called "hardness" and "softness" of the rays. The former are the penetrating and affect tissues, sometimes favourably and sometimes unfavourably, far below the surface. The "soft" rays affect the epidermis. In the use of "hard" X-rays tubes for deep treatment it is necessary to screen the skin with various thicknesses of aluminium or lead, &c. For treatment of skin affections only, there have been no satisfactory means for screening out the penetrating rays, consequently the problem has been the production of "soft" rays with a minimum of "hard" rays. X-ray tube glass is usually a potash or soda-lime silicate. Lindemann found that by substituting lithium for potassium the rays were "softer." He then substituted beryllium for calcium, and finally boron for silicon. Lithium-beryllium-boron glass shows over 30 per cent reduction in the empirical molecular weight. Windows of this glass let into X-ray tubes give the "soft" rays desired. I am pleased to exhibit, through the courtesy of Waite and Bartlett, one of these tubes wherein three "unused" elements were utilised. It would be interesting to see the effect with a potassium-barium-zirconium glass. We know the effect of substituting tungsten for the platinum target within these tubes.

In connection with the above I show you samples of titan-quartz and zircon-quartz glass, for which original properties are claimed. Analyses of such quartz published in the *Chemiker Zeitung* show from 0·05—0·15 per cent of zirconium, and 0·0—0·11 per cent of titanium oxide, so they are what they are not.

Application of the newer electronic conceptions of valence, especially when associated with residual affinity, with the development of methods for changing valence according to our wishes, will unquestionably cause many of these unused elements and many of those now most used to assume new properties. I call your attention to one qualitative illustration. Pure lead does not plate on iron. When molten lead is caused to flow to and fro as a conductor of a low voltage high amperage alternating current for variable periods of time, usually several hours, it then plates iron as may be seen from the sample so plated this week. The lead is pitted and the sample not perfect, but it points a way, which may serve as a hint in seeking uses for such elements as cadmium, selenium, and tellurium.

An indifferent and unsatisfying classification of the "unused" elements has been attempted. Over one-third of the accepted chemical elements are little used. "Rare" elements have been shown to be not so rare. Furthermore, rarity bears little direct relationship to utility. Desire to eat the cake and keep it at the same time are important factors in making use of some of the elements. Illustrations of the development of methods for reducing the cost of production have been cited. Means for stimulating work in utilising elements now available have been suggested. These workers at least could correct much of the misinformation now transmitted by the normal channels from one generation to another. Directions in which real modern physical chemistry has made it possible to use some of these elements and opened up further possibilities have been mentioned. The limited time and assumed patience of our members have forced a degree of unavoidable superficiality.

The Seventh Congress of the International Association for Testing Materials will be held under the Patronage of H.M. the Czar of Russia, in St. Petersburg, from August 12—17, 1915. Four days will be devoted to the discussion of the most important problems on testing materials. After the Congress extensive excursions in the interior of Russia have been arranged. The Offices of the British Section of the Association are at the Iron and Steel Institute, 28, Victoria Street, London, S.W.

CHEMICAL REACTIONS AT VERY LOW PRESSURES.*

I.—The Clean-up of Oxygen in a Tungsten Lamp.

By IRVING LANGMUIR.

(Concluded from p. 257).

Summary.

1. In order to obtain a vacuum so free from water-vapour that a heated tungsten filament will not produce appreciable quantities of hydrogen by the decomposition of the water-vapour, it is necessary during exhaustion to heat the bulb to 360° for about an hour, and to employ either phosphorus pentoxide or liquid air as a drying agent.

2. By this heating about 300 cu. mm. of water-vapour, 20 cu. mm. of carbon dioxide, and 4 cu. mm. of nitrogen are evolved from a 40 watt lamp bulb which could not be removed from the bulb at room temperature by ordinary means.

3. A tungsten wire heated in oxygen at low pressures begins to oxidise at about 800° K, the oxide forming a brown or blue coating on the metal. By heating to about 1200° the oxide volatilises without dissociation and leaves the wire clean and bright.

4. Above 1200° oxygen at pressures below 0·02 mm. acts on a tungsten wire at a rate which is strictly proportional to the pressure of oxygen and is proportional to the surface of tungsten exposed. The rate increases as rapidly with the temperature as do the rates of most chemical reactions at similarly high temperatures. No fatigue effect can be observed, and the past history of the wire does not influence the results. There is much evidence that no film of oxide remains on the metal, but that the oxide distils off to the bulb as fast as formed.

5. The composition of the oxide produced is WO_3.

6. The velocity of the reaction is not affected by varying the temperature of the bulb.

7. The conditions under which this reaction was studied differ in several important respects from those that prevail with reactions at ordinary pressures. Because of the fact that the normal free path of the molecules of the gas is of the same order of magnitude as the dimensions of the bulb, the following unusual conditions prevail:—

(*a*) A molecule of oxygen can strike the filament only once before returning to the surface of the bulb.

(*b*) The velocity of the oxygen molecules is not affected by the temperature to which the filament may be heated. Hence we may say that the metal is made to react with a gas at a totally different temperature from itself—a thing impossible at atmospheric pressure.

(*c*) The product of the reaction, WO_3, in diffusing away cannot influence the rate at which the oxygen comes in contact with the metal, as would be the case at higher pressures.

These facts make it much easier to study the mechanism of the reaction.

8. The rate at which the oxygen molecules come into contact with the surface of the filament was calculated. This rate gives the maximum possible rate of the chemical reaction. The ratio of the actually observed rate to this maximum rate is called ε. The values of ε at different temperatures are given in Table IV. They range from 0·0011 at 1270° K to 0·15 at 2770° K.

9. Applying the principles of the kinetic theory to an analysis of the experimental data, we are led to the following conception of the mechanism of the reaction:—

The oxygen molecules that strike the filament do not react directly with tungsten atoms, but as a first step become negatively charged by taking up an electron from the metal. On the average about 30 electrons in the metal collide with the oxygen molecule during the time that it is in contact with the metal. Only those electrons which

* Paper read before the New York Section of the American Chemical Society. From the *Journal of the American Chemical Society*, xxxv., No. 2.

have a velocity of 62×10^6 cm. per sec. or more succeed in charging the oxygen atoms. When we say that 30 electrons collide with each oxygen molecule, we mean that 30 electrons reach such positions with respect to the oxygen molecule that they would combine with it if their velocities were greater than 62×10^6 cm. per sec. The number of electrons in the metal that have velocities as high as this is so small that only a few of the oxygen molecules that strike the tungsten become negatively charged. For example, with the tungsten wire at 1270°, only one electron out of about 24,400 has a velocity as high as 62×10^6. Therefore the number of oxygen molecules that receive a charge is only 30/24400, or only about one out of a thousand.

The number of electrons in the metal must be at least one-seventh as great as the number of tungsten atoms.

The oxygen molecule, after taking up a negative charge, is held by electrostatic forces to the positively charged tungsten atoms, and soon, by secondary reactions, combines with the tungsten and with oxygen atoms to form WO_3. The present experiments do not throw much light on the nature of these secondary reactions.

This theory accounts quantitatively for the observed values of ϵ between the temperatures 1270 and 1770° K, and for the fact that ϵ does not depend on the temperature of the oxygen. It also leads to several interesting deductions which do not appear to be inconsistent with known facts.

The writer wishes to express his indebtedness to Mr. S. P. Sweetser, who has carried out most of the experimental part of this investigation.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, May 21, 1914.

Sir William Crookes, O.M., President, in the Chair.

Papers were read as follows:—

"*Effect of the Magneton in the Scattering of a-Rays.*" By Prof. W. M. Hicks, F.R.S.

The presence of a magneton in an atom must exert some effect in scattering α- or β-particles passing through the atom. In order to test the order of magnitude of the effect, the orbits of charged particles moving in the equatorial plane of a magneton are discussed, and it is seen that the scattering produced is very considerable. The nearest approach of an α-particle to the centre of the atom is of the same order as in Rutherford's theory. The electrostatic repulsion of an α-particle combined with the magnetic field of the atom will therefore be more effective, as the diminished velocity will render the particle much more susceptible to the magnetic forces.

"*Luminous Vapours Distilled from the Arc, with Applications to the Study of Spectrum Series and their Origin.*" (I.). By the Hon. R. J. Strutt, F.R.S.

1. It is known that mercury vapour distilled away from the arc *in vacuo* remains luminous for some distance away from the region of discharge. It is now shown how to observe brilliant effects of the same kind from a large number of other metals.

2. As the luminous vapour moves away from the region of discharge, the rate at which different constituents in the spectrum die out is not always the same. Thus, for instance, both the subordinate series of lines in the sodium spectrum die out at the same rate, but the principal series dies out more slowly. The lines belonging to any given series always die out at the same rate, but another series may or may not die out at the same rate as the first.

3. In some cases the glowing vapour distilled from the arc shows a band spectrum. The alkali metals show a continuous band beyond the limit of the subordinate series like that seen in absorption in the hydrogen stars.

The present instalment of this investigation deals only with experimental methods of observing the luminous jets of metallic vapour distilled from the arc and their more obvious features. In the next I hope to discuss the effect of an electric field in quenching the luminosity, and the inferences which can be drawn from the observations generally as to the origin of the radiation and its various spectroscopic constituents.

"*On the Ionisation of Gases by Collision and the Ionising Potential for Positive Ions and Negative Corpuscles.*" By W. T. Pawlow.

"*The Determination of Elastic Limits under Alternating Stress Conditions.*" By C. E. Stromeyer.

The present paper deals exclusively with the question of Endurance or Fatigue qualities of metals. The apparently incongruous results obtained by previous experimenters, including those by Wöhler, made it appear probable that samples taken from different parts of a bar or plate might differ so much in quality that the law of fatigue would be masked by local variation of quality. The test pieces of the present first series (*bending*) were therefore shaped in such a manner that consecutive pieces were separated from each other in the original plate by only one inch. The test results were found to be very consistent and could be expressed by the formula $S_n = Fl + C(10^6 : N)^{1/4}$, where S_n is the nominal alternating stress which will cause fracture after N repetitions, Fl is the fatigue limit found by extrapolation from a series of tests resulting in fracture, and C is a constant. A comparison was made of previous tests with the help of this formula, and it was found to agree well with those of Wöhler, Baker and Eden, Rose and Cunningham.

The *torsion* fatigue tests were made with the same materials as used in the above tests, and the results also agreed very closely with the above formula, except that new values for Fl and C were found. A comparison was made between the fatigue limits as found by the bending-fatigue tests and by the torsion-fatigue tests, the ratio between the two averaging about 3 to 2. The comparison between the bending and shearing stresses, which will produce fracture after a certain number of revolutions, has also been made, but is of relatively less value, for these stresses are merely nominal ones and the formulæ which would reduce them to actual stresses are not the same for bending as for torsion.

The enquiry was extended to the measuring of the *heat generated* during fatigue tests. It was found that with low alternating stresses no heat was produced, or, at any rate, so little that it could not be measured, but when certain limiting stresses were exceeded then the generation of heat was quite perceptible. The stresses, at which there was a first indication of heat production, were assumed to be the fatigue limits of the material, for the heat production suggests internal friction and these limits agreed reasonably well with the fatigue limits (Fl) which were found by extrapolation with the help of the above formula.

This calorimetrically-determined fatigue limit was practically a fixed value for any one quality of material, the most interesting case being a crank shaft from which 19 samples were cut. In the first group of three samples cut from the end of the shaft, the minimum and maximum values of the fatigue limit were 11·15 and 11·40 tons per sq. in. In the second group of eight samples cut from between the crank webs, the fatigue limits ranged from 11·30 to 11·60 tons per sq. in., and in the third group of eight samples they ranged from 12·05 to 12·15.

These results agree amongst themselves far better than the tensile tests of the same material, tests which at present are looked upon as reliable indicators of quality.

"*The Emission of Electricity from various Substances at High Temperatures.*" By G. W. C. Kaye and W. F. Higgins.

Experiments have been conducted at temperatures from 2000° to 2500° C. within a carbon-tube furnace at atmospheric pressure. Under these conditions the electrical emissions, in the absence of any applied potential, have been measured for a number of substances (including the alkaline earths and the metals tin, aluminium, iron, and copper) on their introduction into the furnace. During their rapid volatilisation the substances gave out large amounts of electricity which, with one exception, were negative in sign. For example, barium oxide and alumina generated negative currents of the order of 4 ampères per sq. cm., boiling tin about 2 ampères per sq. cm., and boiling iron about 1 ampère per sq. cm. Boiling brass, on the contrary, produced a positive current of about 0·5 ampère per sq. cm. The results have interest in connection with the problems of solar magnetism. Incidentally, striking absorption-colourations of the emitted light from the furnace were observed when the alkaline earths were introduced, *e.g.*, the colour in the case of strontia was a brilliant green, and with baryta a salmon-pink.

CHEMICAL SOCIETY.

Ordinary Meeting, May 7, 1914.

Prof. W. H. Perkin, LL.D., F.R.S., President, in the Chair.

(Concluded from p. 235).

129. "*The Alloys of Aluminium and Silicon.*" By Charles Edward Roberts.

A re-investigation of the thermal diagram of the aluminium-silicon alloys in order to determine the possibility of the existence of either a compound of the two elements dissociating at high temperatures on an allotropic form of silicon stable above 1200°, resulted in a complete confirmation of the results arrived at by Fraenkel (*Zeit. Anorg. Chem.*, 1908, lviii., 154), that the alloys form a simple eutectiferous series, the eutectic melting at 578°.

130. "*The Constitution of Camphene. Part II. Experiments on the Synthesis of Several Degradation Products of Camphene.*" By Walter Norman Haworth and Albert Theodore King.

An account was given of the condensation of ethyl oxalate with ethyl *as*-dimethylsuccinate in the presence of potassium or sodium ethoxide, and of the synthesis of the lactonic acid (IV.) through the following stages :—

$$\begin{array}{l} CH_2\cdot COCl \\ | \\ CMe_2\cdot CO_2Et \end{array} \qquad \begin{array}{l} CH_2\cdot CO\cdot CH(CO_2Et)_2 \\ | \\ CMe_2\cdot CO_2Et \end{array}$$

I. II.

$$\begin{array}{l} CH_2\cdot C(OH)(CO_2Et)\cdot CH(CO_2Et)_2 \\ | \\ CMe_2\cdot CO_2Et \end{array}$$

III.

$$\begin{array}{l} CH_2\cdot C(CO_2H)(CH_2\cdot CO_2H)\diagdown \\ | \qquad\qquad\qquad\qquad\qquad\qquad O. \\ CMe_2 \text{------------} CO\diagup \end{array}$$

IV.

Attention was directed to the fact that a complete synthesis of camphene has now been realised by the combined experiments of several independent workers. Camphenic acid and camphenilone having now been synthesised (*Ber.*, 1914, xlvii., 871, 934), this, considered along with the earlier work of Moycho and Zienkowski (*Ber.*, 1905, xxxviii., 2461; *Annalen*, 1905, cccxl., 58) on the preparation of camphene from camphenilone, establishes finally the constitution of this terpene as represented by Wagner's formula.

131. "*Action of Nitrous Acid on Dimethylpiperazine.*" By Prafulla Chandra Ray.

In continuation of previous investigations on the amine nitrites, attempts have been made to isolate an amine dinitrite. When ethylenediamine hydrochloride or hydrobromide was treated with silver nitrite, it was noticed that even during the initial stages of reaction slight decomposition often set in, with evolution of nitrogen and formation of glycol and ethylene oxide. The aqueous filtrate, on evaporation in a vacuum, gave a non-crystalline residue, which did not dissolve to a clear solution, and on evaluation by the Crum-Frankland and "urea" methods respectively, gave, as a rule, an appreciable excess of gas by the former, proving the conversion of a certain proportion of nitrite into nitrate. In two preparations, however, the nitrogen, as estimated by both the processes, agreed well :—

1. 0·0214 gave 2·1 cc. N_2("nitritic") at 24° and 760 mm. N = 11·0.
2. 0·025 gave 2·6 cc. N_2("nitritic") at 25° and 760 mm. N = 11·34.

The result approximates to a mononitrite, $C_2H_4(NH_2)_2,HNO_2$, which requires N("nitritic") = 13·08 per cent. That the percentage of nitrogen actually found is lower is easily accounted for by the fact that there is always a slight insoluble residue.

It has already been shown (*Proc.*, 1912, xxviii., 258) that whilst benzylethylammonium nitrite can be isolated in a crystalline form, the corresponding methyl compound decomposes even in aqueous solution, mainly into the nitroso-derivative, and that after some time equilibrium sets in, thus :—

$$C_7H_7\cdot NHMe,HNO_2 \rightleftharpoons C_7H_7\cdot NMe\cdot NO + H_2O.$$

It has now been found that by using an alcoholic solution of the amine hydrochloride, this reverse change is completely arrested. The alcoholic solution, when evaporated in a vacuum over sulphuric acid, yields a crystalline mass, which is *benzylmethylammonium nitrite* :—

0·0294 gave 2·46 cc. N_2("nitritic") at 33° and 760 mm. N = 8·94.

$C_8H_{11}N,HNO_2$ requires N = 8·33 per cent.

An alcoholic solution of piperazinium chloride, when similarly treated, gave a salt approximating to a dinitrite. It was thought that dimethylpiperazine might yield better results, and this expectation has been realised. The base chosen was α-2 : 5-dimethylpiperazine, which Pope and Read's recent investigations prove to have the *trans*-configuration (*Trans.*, 1912, ci., 2325; 1914, cv., 219).

The aqueous solution of the hydrochloride, on treatment with silver nitrite and evaporation of the filtrate in a vacuum, gave a crystalline salt, which was found to be *nitrosodimethylpiperazinium nitrite*,—

$$NO\cdot N{<}{\begin{array}{l}CHMe\cdot CH_2\\ CH_2\cdot CHMe\end{array}}{>}NH,HNO_2.$$

0·0286 gave 7·3 cc. NO at 26° and 760 mm. by the Crum-Frankland method, whereas the "urea" test liberated only half the amount of nitrogen (compare *Trans.*, 1913, ciii., 2), whence N = 14·66.

$C_6H_{13}ON_3,HNO_2$ requires N = 14·74 per cent.

It should be mentioned that the aqueous solution of piperazinium chloride, by treatment as above, gave dinitrosopiperazine in the first two or three crops. The introduction of the two methyl groups in the ring had the desired effect of diminishing the tendency towards the formation of the nitroso-derivative.

Dimethylpiperazinium chloride in alcoholic solution was next treated with finely powdered silver nitrite. Although both the reacting substances are very sparingly soluble in alcohol, the increased solubility of silver nitrite in the presence of an amine nitrite (due, no doubt, to the formation of a double salt) facilitates the double decomposition. The alcoholic filtrate was evaporated in a vacuum, and the crystalline salt which was thus obtained was found to be a *dinitrite*, as both by the Crum-Frankland and the "urea" process it yielded the same amount of nitrogen :—

0·023 gave 2·7 cc. N_2("nitritic) at 30° and 760 mm. N = 13·33.
0·0764 (by combustion) gave 18·0 cc. N_2 at 26° and 760 mm. N = 26·41.
$C_6H_{14}N_2,2HNO_2$ requires N("nitritic") = 13·46, and N(total) = 26·92 per cent.

Conductivity measurements also bear out that the one is the nitrite of a nitroso-derivative and the other a dinitrite (compare *Trans.*, 1912, ci., 1555).

Nitrosodimethylpiperazinium Nitrite.

V	252·1	504·2	1008·4	2016·8
μ	93·5	102·7	114·3	120·7

In this case there are only two univalent ions.

Dimethylpiperazinium Dinitrite.

V	200·3	400·6	801·4	1602·4
μ	210·3	225·4	237·2	241·1

Evidently there are three ions in solution. The measurements were conducted at 25°.

132. "*Partially Methylated Glucoses.* Part III. *Monomethyl Glucose.*" By JAMES COLQUHOUN IRVINE and THOMAS PERCIVAL HOGG.

Monomethyl glucose has been prepared from glucose-diacetone on a sufficiently large scale to permit of the α- and β-modifications being isolated in pure stereochemical forms. As the interconversion $\alpha \rightleftharpoons \beta$ proceeds extremely slowly in pure methyl alcohol, it has been possible to determine the initial specific rotation of each form of the sugar with a high degree of accuracy. The mutarotatory changes observed were:—

α-Form (m.p. 160·5—161°). β-Form (m.p. 133·5—135°).
Initial $[\alpha]_D$ +107·6° $\rightarrow \underbrace{68·5°, 68·3°}$ $\leftarrow$ +24·4° initial $[\alpha]_D$.

The difference of the molecular rotations of the α- and β-forms thus equals 16141, and as the corresponding value for glucose is 16200, the result agrees with Hudson's rule (*Journ. Am. Chem. Soc.*, 1909, xxxi., 66) within the limits of experimental error.

It has been found that monomethyl glucose yields few characteristic derivatives, and its methylglucosides, in view of the spatial distribution of the hydroxyl groups, fail to enter into condensation with either acetone or benzaldehyde. A well defined *monomethyl glucoseanilide* was, however, isolated (m. p. 154—155°). This compound shows suspended mutarotation in a remarkable degree, and the optical change $[\alpha]_D$ −108·5° $\rightarrow$ −50·3° was only promoted by traces of acids, and not by alkalis.

The constitution previously assigned to monomethyl glucose has been confirmed, as, on oxidation with nitric acid, the sugar is converted into *monomethyl gluconolactone*, thus indicating that the methoxyl group is attached to a terminal carbon atom. The sugar is not fermented by living yeast, or by yeast extract, and is unaffected by most bacteria which attack glucose. The action of *B. Clocae* (Jordan), however, resulted in the formation of both acid and gas, but the reaction proceeded much more slowly than in the case of glucose.

133. "*Studies in the Diphenyl Series.* Part VI. *The Configuration of Diphenyl and its Derivatives.*" By JOHN CANNELL CAIN and FRANCES MARY GORE MICKLETHWAIT.

It has been found that benzidine and tolidine condense with reagents for ortho-diamines, such as benzil and glyoxal, to form compounds of the type—

$$\begin{array}{l} C_6H_4\cdot N:CR \\ \;| \qquad\quad\; | \\ C_6H_4\cdot N:CR \end{array}$$

(where R = H or C_6H_5).

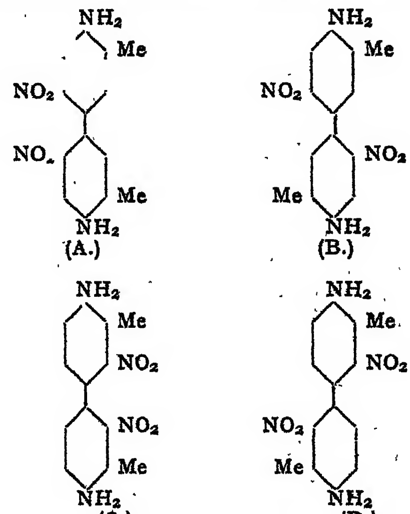
This reaction appears to prove that Kaufler's stereochemical configuration of members of the diphenyl series is correct.

134. "*Studies in the Diphenyl Series.* Part VII. *Isomeric* o- *and* m-*Dinitro-o-tolidenes.*" By JOHN CANNELL CAIN and FRANCES MARY GORE MICKLETHWAIT.

In addition to the *o*-dinitrotolidine (m. p. 270°) described by Gerber, the authors have obtained, by the nitration of diacetyltolidine, a new isomeric *o-dinitrotolidine* (m. p. 202—203°).

By the nitration of tolidine sulphate or diphthalyltolidine there are formed in addition to Gerber's *m*-dinitrotolidine (m. p. 217°; obtained by him from tolidine sulphate), three new m-*dinitrotolidines*, melting at 205—206°, 263°, and 284° respectively.

These four bases are represented by the plane formulæ:—



(A.) (B.) (C.) (D.)

and the possibility of the separate existence of A and B and of C and D, as well as of the two isomeric *o*-dinitrotolidines, is readily explained by means of Kaufler's stereochemical formula for diphenyl.

135. "*Thio-derivatives of β-Naphthylamine.*" By WILLIAM REEVE and SAMUEL SMILES.

The substances here described were obtained in some experiments which had been undertaken with the object of synthesising $\alpha\beta$-naphthathiophen. The results are now published, since the scheme has been abandoned on account of the extremely poor yields of the essential products.

Dimethyl-β-naphthylamine sulphide,—

$$NMe_2\cdot C_{10}H_6\cdot S\cdot C_{10}H_6\cdot NMe_2,$$

was obtained by treating three molecular proportions of dimethyl-β-naphthaline dissolved in light petroleum with one molecular proportion of sulphur chloride. The insoluble hydrochloride of dimethyl-β-naphthylamine separated, and when this had been removed the required substance was isolated by spontaneous evaporation of the solution. After recrystallisation from hot alcohol it was obtained in very pale yellow needles, which melted at 145°:—

Found, S = 8·4. N = 7·2.
$C_{24}H_{24}N_2S$ requires S = 8·6; N = 7·5 per cent.

Di-β-naphthylamine sulphide, $NH_2\cdot C_{10}H_6\cdot S\cdot C_{10}H_6\cdot NH_2$, was obtained by treating β-naphthylamine in nitrobenzene solution at 160° with sulphur in the presence of lead oxide. The solvent was removed in a current of steam, and the residue was dissolved in acetic acid. Water was then added to this solution, and the amorphous precipitate which separated was collected and dissolved in ether. By spontaneous evaporation of the solvent the sulphide was deposited in an impure condition. It separated from solu-

tion in hot alcohol in colourless needles, which melted at 166° :—

Found, S = 10·0 and 9·8. N = 8·6 and 8·7.
$C_{20}H_{16}N_2S$ requires S = 10·1 ; N = 8·86 per cent.

When dissolved in hot aqueous mineral acids, the substance was readily oxidised by atmospheric oxygen, an insoluble blue material being formed.

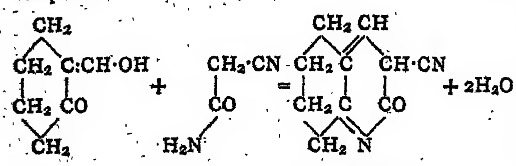
The yield of the sulphide obtained by this method varies considerably, not only according to the quantity of the reagents taken, but also according to other conditions, which have not yet been determined. In the majority of experiments the yield was extremely poor, and in these cases it is difficult to separate the substance from the polysulphides which are always formed. These compounds —the di- and tri-sulphides—have not been closely examined.

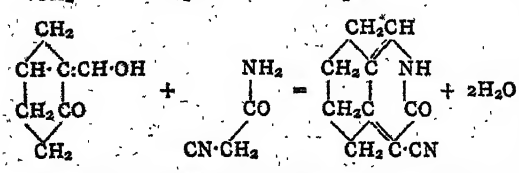
136. "*The Interaction of Naphthasulphonium-quinone and Substances containing the Thiol Group.*" By Brojendranath Ghosh and Samuel Smiles.

A description was given of the reaction of certain thiol derivatives with β-naphthaquinone and β-naphthasulphonium-quinone. From the last-named quinone, thiol and thioglycollyl derivatives of dinaphthathioxin were obtained. The action of alkali with these substances and with hydroxydinaphthathioxin was examined in order to determine whether isomeric change could be induced, as in the case of the *iso*sulphide of β-naphthol. The results were negative.

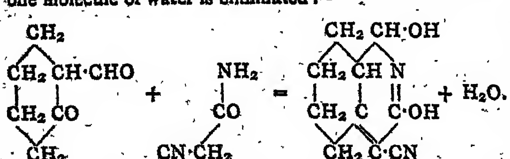
137. "*The Formation of Heterocyclic Compounds from Hydroxymethylene Ketones and Cyanoacetamide.*" (Preliminary Note). By Hemendra Kumar Sen-Gupta.

Hydroxymethylene-ketones condense readily with cyanoacetamide in the presence of piperidine or diethylamine, giving rise to heterocyclic compounds; in the case of open-chain hydroxymethylene-ketones, hydroxypyridine derivatives are obtained, whilst with hydroxymethylene-*cyclo*ketones, substances are produced which may be either quinoline or *iso*quinoline derivatives, according as to whether the condensation commences at the formyl carbon atom or the ketonic carbonyl of the hydroxymethylene compound.





In addition to these condensation products which are formed by the elimination of two molecules of water, there is evidence of the formation of a second type in which only one molecule of water is eliminated :—



In some cases, this intermediate type has been isolated by careful crystallisation. Since a well-defined acid is obtained by hydrolysing either of the condensation products thus produced, there is little doubt as to the similarity of their structures. In a few cases the final products which are deposited from the condensing mixture have found to be those condensation products which have lost two molecules of water.

The following compounds have been obtained :—

1. Ethyl hydroxymethylene-ethyl ketone,—

$$C_2H_5\cdot CO\cdot C(CH_3):CH\cdot OH,$$

gives with cyanoacetamide a mixture of condensation products which, on hydrolysing, yields an *acid*, $C_9H_{11}O_3N$ (m. p. 278—279°); this evolves carbon dioxide on melting, and passes into the *compound*, $C_8H_{11}ON$ (m. p. 136—138°).

2. Hydroxymethylene*cyclo*hexanone yields the condensation products $C_{10}H_{10}ON_2$ (m. p. 250°) and $C_{10}H_{12}O_2N_2$ (melting above 300°). Both *compounds*, on hydrolysis with 80 per cent sulphuric acid, give the same *acid*, $C_{10}H_{11}O_3N$ (m. p. 265°), which evolves carbon dioxide on melting, and passes into the *compound*, $C_9H_{11}ON$ (m. p. 204°).

3. 2-Methylhydroxymethylene*cyclo*hexanone gives the *compound* $C_{11}H_{12}ON_2$ (m. p. 242°), which, on hydrolysis, yields the *acid*, $C_{11}H_{13}O_3N$ (m. p. 260°); this loses carbon dioxide, and forms the *compound*, $C_{10}H_{13}ON$ (m. p. 142°).

4. 4-Methylhydroxymethylene*cyclo*hexanone gives the *compound*, $C_{11}H_{12}ON_2$ (m. p. 228—229°), which is hydrolysed to the *acid*, $C_{11}H_{13}O_3N$ (m. p. 284), and the latter yields the *compound*, $C_{10}H_{13}ON$ (m. p. 206—207°), with loss of carbon dioxide.

Experiments with the object of elucidating the constitution of this class of compounds are in progress.

138. "*Studies of Ammonium Solutions.*" A Correction. By Roland Edgar Slade.

In a former communication it was shown that the potential of an ammonium electrode at 25° was given by the equation—

$$e = e_0 - 0{\cdot}059 \log \frac{p_{NH_3} p_{H_2}^{\frac{1}{2}}}{[NH_4^{\cdot}]}.$$

The value of e_0 was calculated to be −0·486 volt from twelve independent measurements. It has been pointed out to the author by Prof. Auerbach that, in calculating these values of e_0, the pressures of ammonia were, by mistake, expressed in mm. of mercury instead of in atmospheres. This mistake has now been corrected, and the values have been revised in accordance with the later value for the potential of the normal hydrogen electrode. The revised value of e_0 is −0·654 volt.

This value has been compared with other data, and found to be in excellent agreement.

139. "*Thujin.*" By Arthur George Perkin.

Rochleder and Kawalier (*Wien. Akad. Ber.*, 1858, xxix., 10; *Journ. Pr. Chem.*, 1858, lxxiv., 8) isolated from the arbor vitæ (*Thuja occidentalis*) in minute amount a glucoside, thujin, $C_{20}H_{22}O_{12}$, which by hydrolysis yielded dextrose and thujigenin, $C_{14}H_{12}O_7$, the latter subsequently passing into thujetin, $C_{14}H_{14}O_8$. Thujigenin and thujetin are described as yellow crystalline substances, soluble in alkalis with a green colour, and in alcoholic ammonia with a bluish green coloration. A re-examination has now shown that thujin is, in reality, quercitrin contaminated with a trace of a second glucoside, and that the green tint of the alkaline solution of the free colouring matter originates from the latter compound. It is possibly a glucoside of myricetin (*Trans.*, 1899, lxxv., 829), but the amount present in the material now examined was far too small for identification. Incidentally, it has been found that quercitrin melts at 183—185°, much higher than has been usually supposed (compare Herzig, *Monatsh.*, 1885, vi., 877), that the formula $C_{21}H_{22}O_{12}$, assigned to it previously, which it is found to possess when dried in the air or at 100°, is, in reality, $C_{21}H_{20}O_{11},H_2O$, and that it may be obtained in the anhydrous condition when heated at 160°.

140. "*The Rotatory Powers of* d- *and* l-*isoamarine and of their Respective Tartrates.*" By Henry Lloyd Snape.

In a previous paper on "Racemic and Optically Active Forms of Amarine" (*Trans.*, 1900, lxxvii., 784; see also

Proc., xxx., 7), the density was inadvertently omitted in the calculation of rotatory powers. Re-derminations were subsequently made, and the missing factor was included. As before, the bases were dissolved in ethyl acetate, and the tartrates in 90 per cent alcohol.

Each determination of the angle of rotation was made by taking the average of a number of rotations (which fluctuated slightly and irregularly—sometimes falling and then rising, and sometimes conversely) measured at the same time on successive days. The following are the results obtained:—

	c.	$[\alpha]_D$.	Number of determinations.
Dextro-base ($C_{21}H_{18}N_2$) ..	4·500	+69·06	3
Lævo-base	4·581	−68·23	2
Dextro-tartrate of dextro-base	1·357	+113·95	2
Dextro-tartrate of lævo-base	3·377	−93·31	3

As the only polarimeter which was at the author's disposal for the above experiments was a very simple one, and could not be trusted to give very exact measurements, Prof. W. J. Pope very kindly undertook to determine $[\alpha]$ in specimens of the dextro-tartrates of *d*- and *l*-*iso*amarine, and the following are his results, for which the author desires to express his thanks.

In each of the following determinations the quantity of the substance stated was dissolved at 20°, made up to 30 cc., and the solution examined in a 4-dcm. tube at 20°.

d-*isoAmarine* d-*tartrate*, 0·9053 grm. in absolute alcohol.

	Hg violet.	Hg green.	Hg yellow.	Na yellow.
α..	+32·57°	+16·56°	+14·18°	+13·48°
$[\alpha]$	+270	+137	+117	+112

Rotatory dispersions—

Hg violet/Na yellow .. .. .. = 2·416
Hg green/Na yellow .. .. .. = 1·228
Hg yellow/Na yellow .. .. .. = 1·052

0·3097 in 90 per cent alcohol by weight.

α..	+12·34°	+6·29°	+5·38°	+5·12°
$[\alpha]$	+299	+152	+130	+124

Rotatory dispersions, 2·410, 1·229, and 1·051 respectively.

l-*isoAmarine* d-*tartrate*, 0·2390 grm. in absolute alcohol.

α..	−7·55°	−3·68°	−3·15°	−3·07°
$[\alpha]$	−237	−115	−98·8	−96·3

Rotatory dispersions, 2·459, 1·199, and 1·026 respectively.

It will be observed that the corrected values for the D line for the tartrate of the dextro-base in 90 per cent alcohol is 124, which is distinctly higher than was obtained with the imperfect apparatus. Similarly, the value for the tartrate of the lævo-base in absolute alcohol is somewhat higher than was obtained from a solution in 90 per cent alcohol. Probably, therefore, the values given above for the bases are, like those cited in the same table for the tartrates, only aproximately correct.

NOTICES OF BOOKS.

The Viscosity of Liquids. By A. E. Dunstan, D.Sc. (Lond.), and F. B. Thole, B.Sc. (Lond.). London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1914.

The authors of this monograph have done a useful work to science in bringing together the scattered data relating to the measurement of the viscosity of liquids. A good deal of work on the subject has been published, but, on the other hand, there is a great lack of agreement about the methods of measurement to be adopted and the interpretation of the results. The authors have endeavoured to give accurate descriptions of the experimental work which has been done upon the viscosity of pure liquids, mixtures, electrolytic solutions, and colloids, and the monograph contains excellent chapters upon the connection between viscosity and chemical constitution, and the application of the results obtained to the investigation of some problems in organic chemistry, such as the determination of the configuration of the acetaldehyde phenylhydrazones, is described.

The Principles of Inorganic Chemistry. By Wilhelm Ostwald. Translated with the Author's Sanction by Alexander Findlay, M.A., Ph.D., D.Sc. Fourth Edition. London: Macmillan and Co., Ltd. 1914.

In the third German edition from which this English translation has been prepared the early chapters were considerably altered, and additions were made which greatly increased the value of the book as a comprehensive treatise on pure inorganic chemistry. Thus a new chapter was provided on solutions, which treated of the properties and general laws of solutions and the application of these laws in the separation of mixtures, and the phenomena of changes of physical state and the general properties of mixtures were discussed The chapter on radio-active substances have been revised and enlarged by the translator, and gives an excellent *résumé* of the subject.

An Elementary Treatise on the Calculus for Engineering Students. By John Graham, B.A., B.E. Fourth Edition. London: E. and F. N. Spon, Ltd. New York: Spon and Chamberlain. 1914.

The author of this very useful book has a thorough knowledge of the requirements of engineering students and of the difficulties which beginners meet with in the study of the calculus. Throughout the book the application of the principles of the calculus to practical problems is kept in view, and some very interesting typical examples are worked out in full, while the large collection of unworked problems to which only the answers are given will afford the student ample practice. An introduction has been added to the fourth edition, giving a brief outline of the more advanced parts of Algebra and Trigonometry with which the student should be familiar before he begins to use the book, and also enumerating some results and formulæ of co-ordinate geometry.

Baumé and Specific Gravity Tables. By Nat. H. Freeman. London: E. and F. N. Spon, Ltd. New York: Spon and Chamberlain. 1914.

This book of specific gravity tables for liquids lighter than water is particularly well printed and will be found convenient in use. The specific gravities are given to seven figures, and to save the user of the book trouble the difference, and also the difference of the differences, are tabulated.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clviii., No. 51, April 14, 1914.

Gravimetric Analysis of Urea.—R. Fosse.—Xanthydrol is a valuable reagent for the quantitative analysis of urea, with which it forms a definite crystalline product of formula—

$$O{<}^{C_6H_4}_{C_6H_4}{>}CH{-}NH{-}CO{-}NH{-}CH{<}^{C_6H_4}_{C_6H_4}{>}O.$$

This compound is only very slightly soluble, and its molecular weight is seven times as great as that of urea. By elementary analysis it is easy to control both the

identity and purity of the precipitate. The solution of urea is first treated with 3·5 times its volume of acetic acid and then half its volume of alcoholic xanthydrol is added. After an hour the crystalline precipitate is washed, dried, weighed, and analysed. According to another method 3·5 times the volume of acetic acid is added, then half a volume of solution of xanthydrol in methyl alcohol, introduced at intervals of ten minutes. The crystals are collected one hour after the last addition.

No. 16, April 20, 1914.

Action of Sodamide upon Allyl Dialkylacetophenones. General Method of Synthesising Trialkylpyrolidones.—A. Haller and Edouard Bauer.—In order to decompose allyldimethylacetophenone with sodamide one and a quarter times the theoretical quantity of the latter is added to equal volumes of the ketone and benzene. A little water is then added, the liquid is neutralised with acid, saturated with ammonium sulphate, and treated with ether. On evaporation and rectification a product of formula $C_{17}H_{13}ON$ is obtained. It has none of the functional properties of allyldimethyl acetic amide, and from its reactions it is found to be 3.3.5-trimethylpyrolidone. This result is confirmed by synthesis.

Action of Ammonia and Amines on Carbon Subnitride.—Charles Moureu and Jacques Ch. Bongrand.—Ammonia acts immediately and very violently upon carbon subnitride, the product being amino butene dinitrile, $CN—C(NH_2)=CH—CN$. This substance is hydrolysed by dilute acids, the reaction occurring in three stages. Butenol dinitrile is first formed, and at once isomerises into oxalacetic nitrile. This last compound then splits into hydrocyanic acid and cyanacetic acid. The tertiary amines have no action on carbon subnitride. The primary and secondary amines, on the contrary, act on it violently, the products being similar to those obtained with ammonia. They are hydrolysed by dilute acids regenerating the base, and giving hydrocyanic and cyanacetic acids.

Berichte der Deutschen Chemischen Gesellschaft.
Vol. xlvii., No. 6, 1914.

Formation of Red Phosphorus by Oxidation of Phosphorus Vapour.—V. Kohlschütter and A. Frumkin.—Red phosphorus is obtained by the cautious oxidation of phosphorus vapour at the ordinary temperature. If gaseous oxygen is introduced in very small quantities into the saturated vapour a dark red homogeneous and transparent product is obtained, which is the result of the incomplete oxidation of the phosphorus vapour. When part of the oxygen and phosphorus contained in it is split off it is converted into red phosphorus. Thus the primary red product is analogous to the intermediate products which appear during the transformation of white phosphorus by phosphorus iodide and tribromide, but, in the formation of red phosphorus from these, constituents are split off which again react with the white phosphorus.

Action of Sodium Hydrosulphide on Tellurium and Selenium.—L. Tschugaeff and W. Chlopin.—When sodium hydrosulphide or rongalite (the double compound of hypothetical sodium sulphoxylate with formaldehyde) acts on metallic tellurium or selenium in alkaline solution a crystalline hydrate of sodium telluride or selenide is obtained. By benzylation with benzyl chloride or with dimethyl phenyl benzyl ammonium chloride benzyl telluride, $(C_6H_5CH_2)_2Te$, is obtained.

Bulletin de la Société Chimique de France.
Vol. xv.-xvi., No. 7, 1914.

Catalytic Preparation of New Ketones.—A. Mailhe.—When mixed vapours of the toluic acids and hydrocinnamic are passed over ferric oxide heated to 470—480° good yields of the three tolylhydrocinnamyl ketones are obtained. In the same way a mixture of anisic acid and ordinary acetic acid gives anisylmethyl ketone, and other mixed ketones can be prepared similarly.

MISCELLANEOUS.

The Royal Society.—Vol. xiii. of the Royal Society's Catalogue of Scientific Papers is the first of the fourth series, which will comprise the titles of papers published or read during the period 1884—1900, and will conclude the work undertaken by the Royal Society, namely, a complete collection of the titles of papers for the whole of the 19th century. The present volume, which will shortly be published, covers the letters A and B. Vol. iii., Part II. of the Subject Index, arranged under the superintendence of Dr. Herbert McLeod, Director of the Catalogue, will also be ready immediately. It deals with Electricity and Magnetism and contains 23,300 entries, thus making in all 56,644 entries for the subject Physics for the years 1800 to 1900 inclusive.

The van 't Hoff Fund for the Endowment of Investigators in the Field of Pure and Applied Chemistry.—In agreement with the regulations of the van 't Hoff Fund, founded on June 28, 1913, persons interested are informed herewith of the following particulars:—The foundation, whose residence is Amsterdam, and of which the supervision is vested in the Royal Academy of Sciences there, gives from the rents of the Fund every year before March 1, and beginning with March 1, 1915, endowments to investigators in the field of pure and applied chemistry who apply for such an endowment before November 1 next to the Committee charged with considering the applications and awarding the grants. At present this Committee is constituted as follows:—A. F. Holleman, President; S. Hoogewerff; A. Smits; F. M. Jaeger, Secretary. If desirable this Committee may appoint still other members for one year only, to co-operate in judging of the applications made. The names of persons to whom a grant is allowed will be published. The grantees are requested to send to the Committee some copies of the papers relating to the results of their work; but for the rest they are at liberty to choose the manner of publication, as well as the journal, in which they like to publish their results, if only they mention the fact that the research was made with an endowment from the van 't Hoff Fund. The amount available over 1915 is about £67. Applications should be sent, registered by post, to Het Bestuur der Koninklyke Akademie van Wetenschappen; bestemd voor de Commissie van het van 't Hoff-fonds, Trippenhuis, Kloveniersburgwal, te Amsterdam, with a detailed account of the proposed use of the grant, and of the reasons on which the candidates ground their claim.—In the name of the Committee of the van 't Hoff Fund, A. F. Holleman, President; F. M. Jaeger, Secretary.

MEETINGS FOR THE WEEK.

Monday, 8th.—Society of Chemical Industry, 8. "Dickson Centrifuge System of Sewage Treatment," by E. H. Tripp. "Studies on the Reduction of Uranium Oxide," by E. K. Rideal. "Contribution to the Discussion on Paper, 'Bleaching of Chemical Pulp,' by Baker and Jennison, and 'Bleaching Efficiency considered in Connection with Suggested Standard for Testing Bleaching Qualities of Chemical Wood Pulp,'" by C. Beadle and H. P. Stevens.

— Royal Institution, 5. General Meeting.

Tuesday, 9th.—Royal Institution, 3. "Celestial Spectroscopy," by Prof. A. Fowler, F.R.S.

Thursday, 11th.—Royal Institution, 3. "Faraday and the Foundations of Electrical Engineering," by Prof. Silvanus P. Thompson, F.R.S.

— Royal Society, 4.30. (The Croonian Lecture). "Bearing of Cryptological Research on Heredity," by Prof. E. B. Wilson, of Columbia University.

— Biochemical Society, 5.30. (In the Institute of Physiology, University College, London).

Friday, 12th.—Royal Institution, 9. "Some Aspects of the American Democracy," by Hon. Walter H. Page, LL.D., The American Ambassador.

Saturday, 13th.—Royal Institution, 3. "Studies on Expression in Art," by Sigismund Goetze.

THE CHEMICAL NEWS.

Vol. CIX., No. 2846.

THE PREPARATION OF EYE-PRESERVING GLASS FOR SPECTACLES.*

By Sir WILLIAM CROOKES, O.M., F.R.S.

(Continued from p. 267).

Measurement of Infra-red Radiation.

Before I had tried many experiments with the thermopile and black mica another difficulty cropped up. The heat radiated from the Nernst glower gradually warmed up the apparatus, and unless a long time was allowed between each observation I never could get the index ray of light to return to zero. This and the little sensitiveness of the instrument used induced me to try a mercurial thermometer in place of the thermo-pile, all other arrangements being as before. The thermometer was specially constructed with a concave bulb coated with carbon from burning camphor. It was divided into tenths of a degree, the scale being about 9 mm. to a degree.

To test, a selected plate of black mica was permanently fixed in the apparatus between the bulb of the thermometer and the slide containing the glass. First of all, upon lighting the Nernst lamp, the rise in temperature was taken, having only the mica plate between the lamp and the thermometer. The thermometer was observed from a distance through a cathetometer. It was allowed to rise about 1° C., and then with a stop-watch the further rise in sixty seconds was observed. A mean of four observations in this way gave a rise in sixty seconds of—

$$\left.\begin{array}{l}1\cdot75\\1\cdot60\\1\cdot725\\1\cdot675\end{array}\right\}\text{mean } 1\cdot683.$$

In making a determination of diathermancy, glass plates 2 mm. thick were prepared and placed close to the thermometer bulb in a holder having a ¼ inch hole; ten observations were made and the mean taken as the value, which was given in percentages of 1·683.

Thus with glass No. 129; mean rise in sixty seconds $=0\cdot26^\circ$ C.

$$\frac{0\cdot26\times100}{1\cdot683}=15\cdot4^\circ\text{ C.}$$

A mean of ten similar observations gave a value which was taken as the diathermancy of the glass to dark heat. Its athermancy is obtained by subtracting this value from 100. In this way a multitude of glasses were tested, and recently the results have been plotted on a curve which was found to correspond closely with the result subsequently obtained by the radiometer method.

The Radiometer Balance.

In early papers on "Repulsion Resulting from Radiation,"† I showed that the blackened surface of a radiometer was repelled by all the rays of the solar spectrum, from the ultra-violet to a distance at the red end extending far into the ultra red, the maximum intensity being a little distance below the spectrum line A.

An instrument was accordingly made based on the principle of the radiometer, and somewhat resembling the apparatus described in a paper read before the Royal Society in 1875,—"On Repulsion Resulting from Radiation."* It is a torsion balance in which the beam moves in a horizontal plane. Figs. 1 and 2 show the details of the instrument, the latter references being the same in each figure. A B is a thin glass tube, with a bulb at the end, B, and ground flat at the end, A. To the centre of A B is sealed an upright tube, C D, having an arm, E, blown to it for the purpose of attachment to the pump. F G is a very light arm of aluminium carrying at the end, G, a disc of silver-flake mica coated with lamp-black. At the end, F, is a small counterpoise to allow the arm to hang level. H is a glass stopper to the upper part of the tube, C D, which is widened out to form a cup to hold mercury. The stopper in the cup is accurately ground in the tube, as long a surface as practicable being in contact. The horizontal arm is suspended from the stopper by a bifilar suspension of fine quartz fibres, I J, which are attached to the arm F G by an aluminium stirrup holding at its upper end a silvered glass mirror of one metre focus. The vertical tube is blown out and the edges ground flat at the part where the mirror hangs; a flat piece of glass is cemented to it, forming a window through which pass the entering and emerging index beams of light. The end A of the horizontal tube is left open to allow of the adjustment of the arm in its stirrup, and then it is sealed with a flat piece of glass cemented on. The stopper, H, is lubricated with drops of burnt indiarubber so that it can be smoothly rotated to allow the arm to be brought accurately to zero.

Fig. 2 shows the arrangement of the apparatus fitted for testing the samples of glass. The radiometer balance is enclosed in a wooden box having two holes opposite the mirror and the end of the blackened disc at the torsion arm. Great precautions must be taken to avoid all extraneous radiations from acting on the black disc; a slightly conical card tube, as narrow as the angular movement of the ray of light will admit, is attached to the window at K in front of the mirror, S, and another to the bulb at L opposite the black disc.

The heat radiation used in these tests is emitted from a Nernst glower, M, enclosed in a metal box with an open end. In front of the glower is an aluminium screen, N, pierced with a centimetre hole. A shutter, O, can be moved up and down by an arm close to the observer. The shutter screen is made of a piece of cork an inch thick, having on each side a plate of polished aluminium. In this way the heating up of the shutter when it is obscuring the ray from the glower is effectually prevented. At P is a frame for supporting the piece of black mica, and at Q is a sliding carrier holding the piece of glass under examination. This is so arranged that it can be drawn out and another piece of glass put in without causing any jar. Behind the glass is an aluminium screen, R, with a hole in it one centimetre in diameter. The vacuum must be a rather high one, about 40 millionths of an atmosphere.‡

The whole apparatus is closely packed with cotton-wool, so that no radiation can get to the black disc but that which comes through the window opposite. The box containing the radiometer balance is firmly attached to the main wall of the house, to avoid as much as possible interference from vibration caused by movements in the room. A spot of light reflected by the mirror, S, from another luminous source is received upon a graduated screen 1 metre distant in the usual manner.

Testing Synthetic Glasses for Diathermancy.

The mode of procedure is thus:—The mica is put in its place and the lamps started. In about ten minutes the zero is adjusted by means of the rotating stopper. When the spot of light is at zero the shutter, O, is raised, and the extent of the deflection noted. At the end of the first half swing the shutter is lowered, and the whole is left at

* Read before the Royal Society, November 13, 1913. From the *Philosophical Transactions of the Royal Society*, Series A, vol. ccxiv., pp. 1—25.

† *Phil. Trans. Roy. Soc.*, 1876, Part II., vol. clxvi., pp. 355-361.

* *Roy. Soc. Phil. Trans.*, 1875, vol. clxv., Part II., pp. 533-4-5.

‡ *Phil. Trans. Roy. Soc.*, 1876, Part I., p. 301 (The Bakerian Lecture), and *Roy. Soc. Proc.*, vol xxv., p. 305.

rest until the light is again at zero. The glass under test, T, is now put in its carrier and slid into place, and the extent of deflection of the spot of light noted when the shutter is raised. The amount of deflection with the same piece of mica interposed is thus obtained with many different kinds of glass, and from the data the order of obstruction to heat rays can be calculated for each. It is a necessary precaution to verify the readings once or twice, and to allow the spot of light to come accurately to zero. It is inclined to shift if observations are repeated too rapidly, owing to the retention of heat by the blackened face of the radiometer disc, and the consequent repulsion between it and the front of the bulb B. This effect soon goes off if a little time elapses between the different observations.

The deflection of the spot of light when the dark mica alone is interposed gives the effect of the total heat ray, and the lessened deflection when the glass under test is also interposed is a measure of the heat it cuts off. By dividing the scale divisions traversed by the luminous index when both glass and mica are in the path of the heat ray by the number of scale divisions traversed when the mica alone is interposed, the result gives the amount of heat obstructed.

Addition of Absorbing Media to the Soda Flux.

The first point to be settled is the effect of dissolving various metallic oxides by fusion in the clear colourless glass. The metal is added in the form of oxide, nitrate, or other salt, according to which is easiest to obtain pure. Unless oxidation of other ingredients is to be avoided the nitrate is preferred, as the copious liberation of gas during the fusion stirs up the fused mixture and assists in making it homogeneous in a much shorter time.

To be generally useful, it is desirable to obtain a glass which will absorb rays of longer wave-length than about λ 7200, and so cut off dark heat radiation. It should also be opaque to wave-lengths shorter than about λ 3550, thus cutting off the most chemically active rays, and also those which give rise to ionisation, *i.e.*, cause the air through which they pass to conduct electricity.

Working in a vacuum and with sensitive plates of emulsion containing no gelatine, Dr. Schumann succeeded in photographing ultra-violet rays as short as λ 1000. In a paper recently read before the French Physical Society by MM. Karl Stockhausen and Fritz Schanz, it is stated that the harmful action of light on the eye is due to the ultra-violet rays. It is also shown that the cornea is opaque to rays shorter than λ 3200.

The crystalline lens is opaque to rays shorter than λ 3500, and rays of longer wave-lengths than this reach

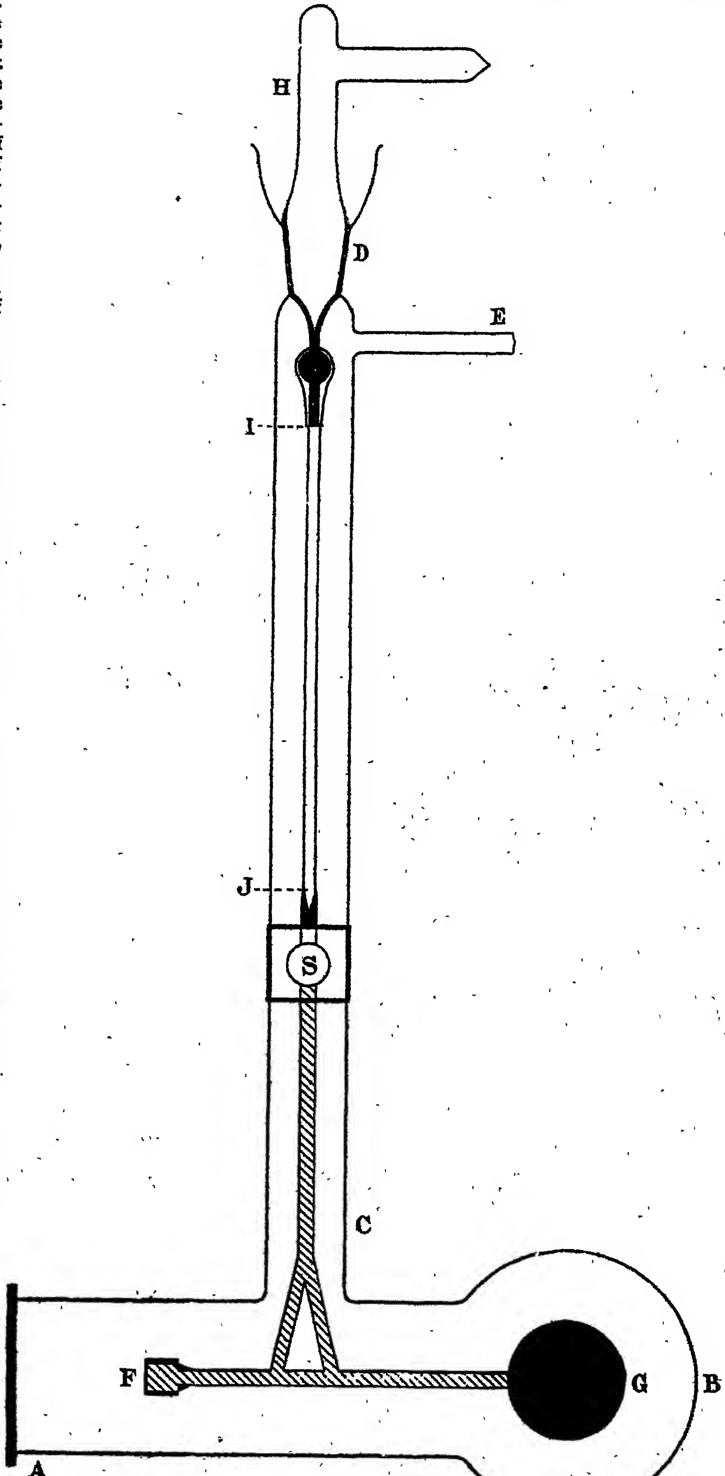


Fig. 1.

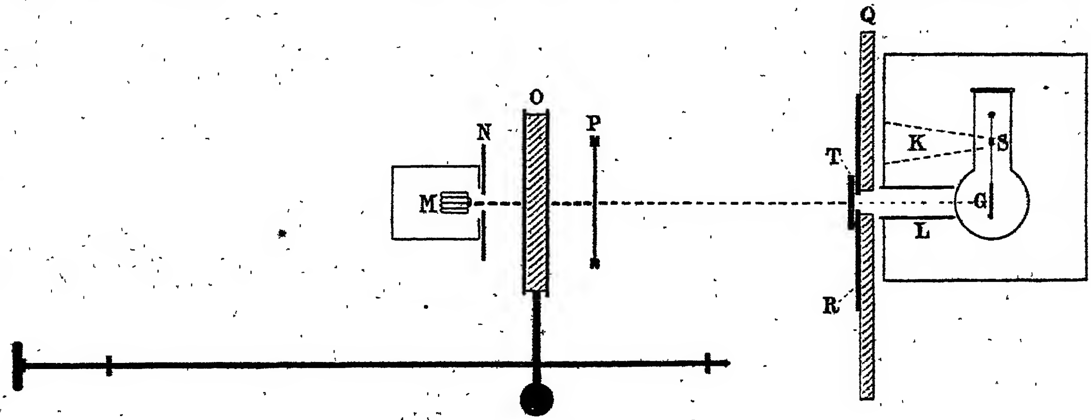


FIG. 2.

A, B, C, D, E. Case of radiometer (Fig. 1).
F, G. Radiometer arm with blackened mica disc.
H. Ground glass joint (Fig. 1).
I, J. Quartz fibres (Fig. 1).
K. Guard tube in front of mirror S.
L. Guard tube in front of radiometer disc.
M. Nernst glower.
N. Aluminium screen.
O. Shutter.
P. Black mica screen.
Q. Carrier for holding glass specimen.
R. Aluminium screen.
S. Concave mirror, one metre focus.
T. Glass specimen under examination.

the retina. As the transparency of ordinary spectacle glasses is limited to λ 3000, it follows that a considerable amount of ultra-violet radiation may reach the cornea through ordinary spectacles.

Method of Testing Glass.

Single metals were at first tried in varying quantities to see if from the colour and properties communicated to the glass they were worth further examination. Each specimen is cut and polished into a plate 2 mm. thick. The plate so prepared is first tested in the spectrum apparatus to ascertain the upper limit of transmission of the ultra-violet rays. It is next put into the radiometer balance to see the percentage of heat cut off, then tested in Chapman Jones's opacity balance* to see the percentage of luminous rays transmitted, and finally the colour is registered in a Lovibond's tintometer.†

A large proportion of the known metallic elements were tested in this manner, and a considerable number were proved to be unsuitable. After experiments extending over several months the following elements were selected as likely to be worthy of further experimentation by combining the metals two, three, or four at a time in one glass so as to enable the advantages of one to make up for the shortcomings in another.

Cerium.	Manganese.
Chromium.	Neodymium.
Cobalt.	Nickel.
Copper.	Praseodymium.
Iron.	Uranium.
Lead.	

I will now take the metals selected for further trials, and give the results of the preliminary test of the glasses so as to ascertain their behaviour in the four instruments above described.

Cerium.

One of the most important additions to soda flux is ceria, which gives a practically colourless glass. Cerium nitrate was generally used, and occasionally cerium borate and ceric oxide. Trial glasses were made, the proportion of metal varying from 1 per cent to 7·5 per cent. The conclusion arrived at on tabulating and considering the results shown by this series of glasses, is that cerium is of value in cutting off the ultra-violet rays. The glasses are very slightly coloured, and allow nearly all the luminous rays to pass. The heat absorption is about 30 per cent, and does not vary much with the amount of cerium present.

Chromium.

This metal, in quantities of less than 1 per cent in the glass, exerts a strong action on the ultra-violet rays, cutting them off down to the blue (λ 4550). In larger proportions, either singly or mixed with other metals, the absorption extends as far as λ 5600 (about the middle of the green). Its heat obstructing power is not on a par with that of uranium, being about 30 per cent for 1 per cent of chromium metal. The luminous rays transmitted by chromium glass containing 0·85 per cent of metal are 37 per cent of the total light, the colour of the glass being green.

Cobalt and Nickel.

Cobalt colours glass a rich blue, and then transmits ultra-violet rays of shorter wave-length than about λ 3200. It cuts off 40 per cent of the heat, and unless in very small quantity obstructs too much light to be of use. Nickel colours glass brown. In glass its absorption of ultra-violet light is about the same as cobalt. It obstructs a little more heat and is more transparent to light. These two metals separately are of no use for the present purpose, but united they have the valuable property of neutralising each other's colour and giving the glass a neutral grey tent.

It is noteworthy that the colours of nickel and cobalt in aqueous solution are green and pink, whilst in solid solution in glass they are brown and blue, in each case complementary to one another.

Solutions of nickel and cobalt sulphates, containing 5 grms. to 100 cc. of water, mixed together in the proportion of 2·5 cc. Ni to 1 cc. of Co, gave a mixture of a neutral grey colour. The mixture was divided into two parts; one was gradually heated to the boiling-point, while the other was left for comparison at the temperature of the laboratory (16° C.). Compared with the cold

* "An Opacity Balance," by Chapman Jones (*The Photographic Journal*, vol xxiii., p. 99).

† The tintometer is an instrument devised by Mr. Lovibond (Messrs. Gallenkamp and Co.). Any colour can be matched by a combination of three sets of glasses, coloured respectively red, yellow, and blue, and numbered in order; the depth of colour increasing with the magnitude of the numbers.

solution, the one at the boiling-point was decidedly pink, and it required a further addition of nickel solution to restore the neutrality of colour at the boiling-point, raising the proportion of nickel to cobalt 3·5 to 1 at 100° against 2·5 to 1 at 16°. As the hot solution cooled the neutral tint gradually changed until it became decidedly green.

The same mixed solution, neutral tinted in the cold, was acidulated with sulphuric acid. It immediately assumed a very faint tinge of pink, but not so decided a tint as the same neutral coloured solution took when heated to the boiling-point.

A solution was prepared containing nickel and cobalt in the proportion of 2·5 to 1; it was evaporated to dryness and ignited. The mixed oxides were then added to the hard soda flux, and the whole melted together at a high temperature; the glass resulting was cut and polished into a plate 2 mm. thick. It was decidedly blue, although the metals were in the proportion to give neutrality at the ordinary temperature when in aqueous solution. More nickel was added in small proportions at a time, and it was not until the proportion in the glass was 1 cobalt to 5 nickel that a neutral grey glass was obtained.

As a colouring agent cobalt is stronger than nickel. It is not easy to get an exact proportion, as the neutral point is difficult to hit with accuracy. If 4 of nickel instead of 5 are used with 1 of cobalt the glass is of a decided bluish tint, while if 6 of nickel are added the colour is brown.

(To be continued).

THE INFLUENCE OF THE ADDITION OF HEDYCHIUM PULP TO CHEMICAL AND MECHANICAL WOOD PULPS UPON THE PHYSICAL QUALITIES OF PAPER PRODUCED THEREFROM.

By CLAYTON BEADLE and HENRY P. STEVENS.

HITHERTO, in the various published investigations on the subject of *Hedychium coronarium*, the results recorded have to do with papers of various kinds, qualities, and substances made from the fibre alone or, in some few instances, with the addition of clay. No results have been published with a view to ascertaining the effects of using *Hedychium coronarium* in admixture with other paper-making fibres. In a paper mill where a commercial trial was made of *Hedychium coronarium* paper of the strong Manila quality, it was decided, subsequent to the production of the Manila paper, to mix some of the beaten *Hedychium coronarium* pulp with long-fibred sulphite pulp. This gave rise to a very strong paper possessing qualities somewhere intermediate between those of strong sulphite and strong Manila. As Hedychium has the property of self-sizing pulp, we thought it would be as well to ascertain whether it imparts these self-sizing qualities to other fibres when used in admixture with them. Also, whether, on the addition of considerable quantities of clay, the paper still retained its sizing qualities.

Certain physical qualities of clay loaded Hedychium papers have recently been dealt with ("The Effects of Mineral Loading upon the Physical Qualities of 'Hedychium' Paper," *Journ. Soc. Dyers and Colourists*, March, 1914, xxx., No. 3), at considerable length. Clay loaded Hedychium papers of the percentage compositions given in Table A were examined to ascertain how far they remained inkproof. It is well known that all ordinary fibres, in order to render them inkproof, have to be sized with rosin (or gelatin), and that the addition of clay calls for an increased consumption or rosin in proportion to the amount of clay retained, that is if the loaded papers are to retain as great an inkproof quality as that of the unloaded.

TABLE A.

No.	Date.	Hedychium.	Clay
1.	December 16, 1913	100·0	0·0
2.	"	91·5	8·5
3.	"	85·0	15·0
4.	"	82·7	17·3
5.	"	73·2	26·8
6.	"	68·6	31·2
7.	"	57·7	42·3

No. 1, consisting of Hedychium and containing no loading, behaves towards ink very much like a strong Manila paper, that is, a broad ink mark showed the liability of repelling the ink on the surface somewhat. The same liability is to be noticed with some very hard tub sized papers. This is a general indication of hard sizing.

No. 2, which contains 8·5 per cent of clay, behaves very similarly, but repels the ink on surface in a somewhat less degree.

No. 3 also, although in the case of 3 the ink spreads in a more normal fashion.

All these are very resistant to ink penetration.

No. 4, containing 17 per cent of clay, shows great resistance to penetration of ink, but the ink spreads on the surface in a uniform manner more like that of a normal paper, and the same may be said of Nos. 5 and 6.

No. 7, which contains 42 per cent of loading, which is an exceedingly high percentage, and with ordinary paper stock would require a large amount of rosin in order to render it properly inkproof, does not show the least penetration to the other side for ordinary substances, and, when Stephens' blue-black ink is used, which we use as a standard, shows practically uniform spreading on the surface and no appearance whatever of penetration to the other side for normal thicknesses.

TABLE B.

Composition.		Bursting strain in lbs. per square inch.	
Hedychium. Per cent.	Mechanical A or chemical B. Per cent.	A.	B.
100	0	64·5	58·3
90	10	65·0	67·0
80	20	63·0	63·0
70	30	65·0	60·3
60	40	60·1	68·3
50	50	55·0	70·0
40	60	50·0	66·1
30	70	44·0	61·6
20	80	38·6	58·1
10	90	31·0	61·4
—	100	29·0	54·6

These results, therefore, show that the influence of the parenchyma cells of the Hedychium is so great as to enable papers to be loaded with clay up to the extent of 40 per cent without breaking down the self-sizing qualities. This is in itself a valuable property. It must not furthermore be lost sight of that with most paper-making fibres it would be practically impossible to retain such a large percentage of clay, even with the aid of rosin sizing.

Mixtures of Hedychium pulp and mechanical wood pulp were made of compositions as per Table B. Similar mixtures were made of Hedychium pulp and chemical wood pulp. Papers were made from each of them and carefully tested by ink tests. Papers prepared from the Hedychium mechanical mixtures were also tested by ink tests. Down to mixtures containing 60 per cent Hedychium and 40 per cent mechanical wood, there was no appearance whatever of penetration or spreading upon the surface. In fact such mixtures appear to behave, as regards ink bearing and ink spreading, in the same manner as 100 per cent Hedychium. At 50 per cent Hedychium and 50 per cent mechanical wood there is a slight disposition to spreading laterally, *i.e.*, at right angles to the ink mark, in feathers upon the surface but with practically no penetration. At 40 per cent Hedychium and 60 per cent mechanical wood the

feathery spread on the surface is augmented. At 30 per cent Hedychium and 70 per cent mechanical wood the ink penetration to the other surface is distinctly marked, and both the feathering and the penetration increase with increased quantities of mechanical; thus 80 per cent mechanical more so than 70, and 90 per cent more so than 80 per cent, and, of course, 100 per cent mechanical is quite soft and liable to immediate penetration.

Taking the case of Hedychium-chemical wood pulp mixtures when tested in a similar manner to the above show very surprising results. All of them show no spreading and no penetration. The breaking down in ink bearing qualities is between the paper showing 10 per cent Hedychium and 90 per cent chemical wood, and the 100 per cent chemical wood paper.

It is evident, therefore, that not only has Hedychium when in admixture with clay, mechanical and chemical wood, marked strength-giving and such like qualities, but it acts as a sizing agent as well as a mineral retainer, and the proportion necessary to produce self-sizing will depend not only upon the proportions (percentage compositions) of Hedychium with these other substances, but upon the nature of the substances with which it is mixed. Thus with chemical wood-pulp, a small amount of Hedychium only, such as 10 per cent, is sufficient to produce self-sizing; with mechanical it is at least 50 per cent, and perhaps somewhere about the same proportion with clay.

Table B is also intended to show the influence of admixture of Hedychium with (*a*) mechanical or (*b*) chemical wood pulp upon the bursting strain of the papers produced. The first two columns indicate the compositions, the third column relates to (*a*) mechanical, and the fourth to (*b*) chemical. The bursting strain is expressed in lbs. per square inch and, for purposes of comparison, is reduced to a standard substance. Each result given in the table is a mean of ten tests. Attempts are always made in such trials to arrive at a uniform substance so as to avoid any further calculations, but where they differ from uniform substances they are calculated to a uniform substance.

Tests were also made (not given in table) of the breaking length of these papers. The results as regards breaking length do not indicate anything particularly striking.

Hedychium for these purposes is beaten fairly short in order to make it operate more as an agglutinating agent than as a fibrous material, and, in each case of that used in admixture with chemical wood, it was so beaten that the bursting strain of 100 per cent Hedychium was made to correspond as nearly as possible with the bursting strain of 100 per cent chemical. Taking the case of the bursting strain of the Hedychium-mechanical mixtures, it will be noticed that the 100 per cent Hedychium has more than doubled the bursting strain of the 100 per cent mechanical. From the results of the top members of the series, there is no evidence of diminution in the bursting strain until the composition arrives at somewhere between 70 per cent and 60 per cent Hedychium and 30 per cent to 40 per cent mechanical. After this point as the percentage of mechanical increases so the bursting strain diminishes.

Hedychium is a pulp which stands the admixture of a certain proportion of other material much inferior to itself without showing deterioration, at least so far as bursting strain is concerned. This is borne out in the Hedychium-mechanical mixtures; it has been observed in cases of admixture with clay, and it is also borne out when one comes to look at the figures obtained with admixtures of Hedychium and chemical wood pulp in which the unmixed chemical wood is only slightly inferior to the unmixed Hedychium. Here it will be observed that, from 100 per cent Hedychium up to 50 per cent Hedychium and 50 per cent chemical, there is a distinct rise in bursting strain, 100 per cent Hedychium being 58 and the 50 per cent being 70, after which there is a distinct fall. We can only account for these results by assuming that there is in the normal Hedychium pulp a surplus of parenchyma cells, that is, more than is required for giving to the Hedychium fibres proper their necessary strength and self-sizing qualities, so that on the addition thereto of any foreign fibre a mixture may be obtained which possesses greater strength or greater bursting strain than the strength-giving constituent, namely, the Hedychium. This is a distinctly valuable property, especially in cases where it is desired to blend Hedychium with other paper-making fibres. Not only is this property to be noted so far as the bursting strain is concerned, but also the breaking length. Thus the mean breaking length of the unmixed Hedychium and chemical, that is, when each unmixed paper is tested and the mean taken for both, is 4·5 kilometres. One would assume in the ordinary course of events that all mixtures of the two would fall somewhere between the figure obtained for the unmixed Hedychium and that obtained for the unmixed mechanical. As a matter of fact, the unmixed Hedychium shows 4·0 kilometres breaking strain, and that containing 80 per cent Hedychium and 20 per cent chemical is 6·0 kilometres. Therefore much stronger paper is obtained by mixing the two than from either of the constituents separately. We wish, however, to point out that far stronger papers are obtainable alone than any of those recorded above when the material is *suitably beaten for the purpose, i.e.*, when Hedychium is beaten for long and hairy papers or krafts. Thus the greatest strength so far obtained is somewhere between 10 and 11 kilometres. The Hedychium pulp here used is prepared in such a way as to act as an agglutinating, compacting, and self-sizing agent, and as a mineral retainer. At the same time in some respects it possesses qualities which are quite equal to those of the strong krafts. When, however, the Hedychium and chemical pulps are blended with large proportions of chemical, as, say, equal weights of each, although the bursting strain is very high, the breaking length found is almost exactly that calculated, the observed being 4·77 kilometres and the calculated 4·5 kilometres.

When a fibre is investigated for the first time it is desirable to examine the qualities of paper producible from it without admixture with other fibres, but inasmuch as the qualities of mixtures cannot be inferred and the paper maker works mostly with blended fibres, it is important as a further step to test the qualities of various mixtures. This communication is for the purpose of recording the influence of such mixtures.

THE ESTIMATION OF CARBON DIOXIDE IN THE AIR.—A SIMPLE AND EXPEDITIOUS METHOD.*

By W. M. DOHERTY, F.I.C., F.C.S., Government Laboratory, Sydney, New South Wales.

The rapid estimation of carbon dioxide in the air of rooms, public halls, factories, or wherever numbers of persons congregate in confined spaces, is sometimes very desirable. The older methods in use are comparatively slow, and in some cases cumbrous. The process I now propose to use, though not perhaps as absolutely accurate as more lengthy methods, is quite near enough for all practical purposes of the hygienist. It is extremely simple, and may be carried out well within the hour from obtaining samples, and in as small a quantity as 100 cc. It is as follows:—

A series of 100 cc. flasks (say, ten in number), well stoppered and filled with water free from carbon dioxide, &c. (preferably distilled water), are emptied at the place where the sample is required to be taken. The stoppers are inserted and the samples taken to the laboratory or tested on the spot. Into each 100 cc. flask a standard solution of sodium carbonate coloured with phenol-phthalein is rapidly run, in arithmetically progressive quantities until a limit is reached beyond which it is unnecessary to go.

* "Report of the Australasian Association for the Advancement of Science, Section B (Melbourne Meeting)," vol. xiv.

For instance, in the first flask 4 cc. are placed; in the second, 5 cc.; in the third, 6 cc.; and so on. Two or three flasks should be reserved for final adjustment if necessary. The standard solution of sodium carbonate is of such a strength that each cc. is equivalent to 0·01 cc. of carbon dioxide. (As the air contains normally about 0·04 per cent of CO_2 it will be seen at once why I begin with 4 cc. of the standard solution). The only factor in the process which requires special care is the making-up of the standard solution. The calculation and equation used in doing this are here given :—

$$1 \text{ cc. of } CO_2 \frac{44}{22320} = 0{\cdot}001971 \text{ grm.}$$

and according to the equation

$$CO_2 + H_2O + Na_2CO_3 = 2NaHCO_3$$

1 cc. of CO_2 converts $\frac{0{\cdot}001971 \times 106}{44} = 0{\cdot}004748$ grm. of Na_2CO_3 into $NaHCO_3$.

Thus a solution is made by dissolving 0·4748 grm. of sodium carbonate in 100 cc. of water, a ½ grm. of phenolphthalein being added as the indicator. This solution is carefully adjusted to its proper strength by titration with N/10 acid in the usual manner. If properly made, 1 cc. will equal 1 cc. of carbon dioxide (N.T.P.). It can be kept for months unimpared. The working solution is made by diluting this 100 times with distilled water free from CO_2, say, 10 cc. to a litre. A standard solution is thus obtained, 1 cc. of which is equivalent to 0·01 cc. of CO_2. The 100 cc. flasks containing the air to be tested and the standard solution are well and continuously shaken for twenty minutes. The amount of CO_2 expressed in percentage by volume is readily indicated by the number of cc. of standard solution decolorised. This lies between the last decolorised flask and the next in the series which retains its pinkness. A reserved 100 cc. sample can finally be tested with half a cc. more standard solution than was required by the decolorised flask. A correction for actual volume in the 100 cc. flask is made, subtracting, of course, the volume of standard solution added.

It remains but to add that ordinary care will have to be exercised in protecting the standard solution from the natural action of the air surrounding it. This can be done in the burette by the aid of a soda-lime filter, the burette being preferably large enough for the whole set of experiments. The solution may also be conveniently kept in an ordinary separator similarly protected. I do not find, however, that using reasonable expedition in pouring the solution into the burette and in running it into the flasks there is any appreciable alteration in its strength.

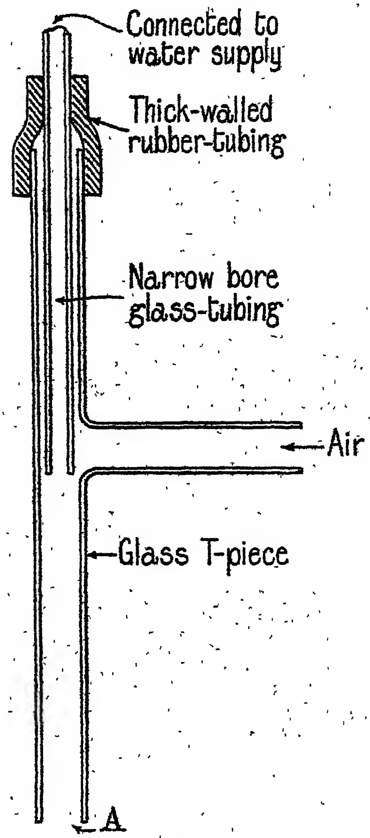
AN IMPROVISED WATER PUMP.

By K. EVANS.

It often happens in a laboratory that a water pump is not always at hand, the available ones being in use or fixed to the water supply at a distance from the apparatus where it is required. The pump described may be of some use in such a case, and may be put together in a few minutes.

A piece of narrow bore glass tubing is inserted in the long arm of a T-tube (glass), the end projecting about ½ in. beyond the junction of the short arm of the T-tube. The inner tube is fixed into the T-tube by means of a piece of thick rubber pressure tubing, the outer end of the tube being attached to the water supply by means of pressure tubing.

A pump so fitted was capable of a suction of 20—30 cubic feet per hour when attached to the ordinary water supply. The pump can be used to produce a gentle suction, by



substituting for the water supply of the mains, a flow of water from a suitable vessel such as a constant-level tank. In this case a long piece of glass tubing is attached to the T-piece at A to act as a fall-tube.

Tanycoed, Carnarvon.

THE SCIENTIFIC WEEK.

(*From Our Own Paris Correspondent*).

FORECASTS OF THE WEATHER.

It is generally said that meteorology is an uncertain science. It progresses slowly. However during the last few years meteorology has made some precious discoveries. Among these discoveries we must include the new method of foretelling the weather imagined by a meteorologist of Caen, M. Gabriel Guilbert. This method, founded on the observation of the wind both in its direction relative to the cyclonic and anticyclonic centres, as well as in its speed relative to the barometric gradient, may be summed up in the two following propositions :— (1) The variation of pressure is determined twenty-four hours in advance by the direction and the actual speed of the surface wind ; (2) the formation of cyclones and their destruction are connected in all seasons only to the surface wind, to the exclusion of upper currents and naturally to mountain winds. In a paper presented to the Academy of Sciences by Prof. Violle, M. Gabriel Guilbert indicates the results of a long series of forecasts made from October 1, 1912, to May 1, 1914. These previsions, numbering 9000, contain indications as to the rise of the barometer and the future of depressions, sometimes even the designa-

tion of the points or limited regions on which was to take place the next day, the maximum barometric rise or fall, and the approximative numerical value of this maximum. The forecasts relating to the variations of pressure have been realised in the proportion of 86 per cent. Those concerning the future of cyclones have had 89 per cent of successes. And the discussion on the non-successes shows that those really due to the rules of the method do not exceed 2 or 3 per cent. The method then would be verified theoretically from 95 to 98 times per 100.

MARINE CHETOGNATES.

Chetognates are worms, but exclusively marine and pelagic worms. On the outside they resemble a small rigid and transparent war torpedo boat. They swim quickly and straight ahead. M. Joubin, Professor at the Natural History Museum, has just studied them in a paper presented before the Academy by the Prince of Monaco. Several thousands of chetognates were captured during the oceanographic cruises of the Prince. They usually live at a depth varying from 1200 to 4000 metres. The species that live in the mean depths come to the surface at night. A curious fact is that the teeth and hooks of these worms become stronger as the depths at which they live is greater. This is because the marine vegetation becomes poorer in the greater depths; the detritus does not descend into the depths of the abyss. The animals are obliged to live on each other; the strongest devour the weaker; the strongest armed triumph. This is why the chetognates that live at a depth of 4000 metres are more powerfully armed than those that live nearer the surface.

THE 26TH SCIENTIFIC CAMPAIGN OF THE PRINCE OF MONACO.

From July 22 to October 10, 1913, the oceanographic cruise commanded by the Prince of Monaco pursued the course of its operations between the coasts of Europe and those of North America. The oceanographers of the *Hirondelle* wished especially to determine precisely certain observations that they had made the previous year concerning a whole series of animals inhabiting depths below 1000 metres and which are to be found, but only during the night, at 200 metres from the surface. The importance of such a fact is considerable from a physiological point of view, for it allows us to catch a glimpse, or at least to suppose, in these animals an extraordinary facility to undergo, twice in twenty-four hours, the enormous decompression of an ascent equivalent to one or several hundreds of atmospheres, and immediately afterwards the recompression to the same atmospheres. This fact also throws a new light on the existence of the fauna that, in spite of the smallness of its individual members, executes every night, and by the simple means of swimming, followed by a vertical fall or drop, this ascension of one or several kilometres. The great progress realised by the campaign of 1913 consists in the regulating and the employment of a very precious instrument constructed by Schäffer and Budenberg, of Madgeburg, to obtain, by a very precise registration, the curve of the depths visited by the net to which it had been joined. The comparison of the lengths of cable let out, and the speeds of the drawing, with the hours and the depths registered, enables the establishment of a law to regulate the work of the net at the depth that is required, in spite of the complications of such an undertaking. But certain difficulties of details still remain, and these will doubtless be overcome during the next campaign; and then we shall be able to know with an absolute precision the level inhabited or passed through, at the different hours of the day and of the night, by these animals that are so marvellously constructed. But it will still remain to be known why they thus make this regular displacement. It was the Naval Lieutenant Bourée who directed this part of the work. M. Albert Ranc, assistant at the laboratories of the Sorbonne, continued, during this cruise, the researches on the physiology of fishes, previously begun by him on board the *Hirondelle*, and concerning the presence of sugar in the blood of marine animals. Many other studies interesting to oceanography were pursued as usual, but those quoted above held the first place. We can, at present, remark a certain decrease in the number of operations executed during the oceanographic campaigns of the Prince of Monaco. This is owing to the fact that about 5000 stations having already been made on the Northern Atlantic during the twenty-nine years that these cruises have been prosecuted, a very advanced knowledge in this domain is already acquired. Henceforth it is necessary to cover wider spaces or to give greater amplitude to certain operations in order to complete certain work or to fill up gaps or desiderata.

THE SEARCHING FOR SMALL PLANETS.

M. Louis Fabry, astronomer at the Observatory of Marseilles, proposes two methods to find little planets at each new opposition. In one method, he determines an elliptic orbit by four observations, two of which are made in the preceding opposition, the two others in that which has preceded it. In the other method he utilised four observations in four different oppositions; in this case he calculates summarily the perturbations produced on the planet by Jupiter by considering the orbit of the planet as circular. The second method has been applied by M. Fabry to the planet 308 Polix, the first by M. Henri Blondel, of Marseilles, to the planet 89 Julia. The two planets were found in the places foreseen or nearabouts at a distance of, say, one or two minutes of an arc.

A NEW COMET.

M. Chofardet, astronomer of the Observatory of Besançon, from May 19 to 22 made four observations of the new comet Zlatinsky. On May 19 it was estimated to be of the fifth magnitude, with a brilliant round head, of four minutes in diameter, with a strong central condensation of from four to five seconds thick. A not very luminous tail, thin and rectilineal, stretched as far as one degree from the head at an angle of 17° to the neighbouring pole.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, May 21, 1914.

Prof. W. H. PERKIN, LL.D., F.R.S., President, in the Chair.

THE PRESIDENT announced that in connection with the van't Hoff Memorial a Fund has been established for the endowment of research in the field of Pure and Applied Chemistry. The amount available during 1915 for purposes of research is about £67.

A Committee consisting of Prof. A. F. Holleman (President), Prof. S. Hoogewerff, Prof. A. Smits, and Prof. F. M. Jaeger (Secretary), has been appointed to award grants. Applications for grants should be sent before November 1, 1914, by registered post to "Het Bestuur der Koninkklyke Akademie van Wetenschappen; bestemd voor de Commissie van het 'van't Hoff fonds' Trippenhuis, Kloveniersburgwal, te Amsterdam," and applicants are requested to submit a detailed account of the manner in which they propose to spend the grant.

Papers embodying the results of the Research may be published in any journal, but acknowledgment must be made of the source of the grant. Copies of the papers embodying the results of the Research must be forwarded to the Committee.

Messrs. L. J. Hudlestone, A. U. Newton, B. N.

Ghosh, T. E. Hodges, G. P. Furneaux, A. Coulthard, A. Baxter, R. O. Bishop, and S. M. Bosworth were formally admitted Fellows of the Chemical Society.

Certificates were read for the first time in favour of Messrs. Frederick George Henderson, 44, Dene View, Wallsend-on-Tyne; Victor Henri, 8, Rue du Puits de l'Ermite, Paris; Robert Ernest Machin, B.Sc., 5, Redcliffe Road, South Kensington, S.W.; Thomas William Thompson, M.A., Queen Elizabeth's Grammar School, Gainsborough.

A Certificate has been authorised by the Council for presentation to ballot under By-law I. (3) in favour of Mr. Probodha Chundra Chattopadhyay, M.A., 90, Maniktala Main Road, Harrison Road P.O., Calcutta.

Of the following papers, those marked * were read:—

*141. "*Ionisation and the Law of Mass Action. Part III. Utilisation of the Osmotic Data and a New Dilution Law*." By WILLIAM ROBERT BOUSFIELD, K.C.

Excellent freezing-point and vapour-pressure data for concentrated solutions of lithium chloride exist, and less complete data for sodium and potassium chlorides, the vapour-pressure data ranging from 40° to 100°. An empirical vapour-pressure formula of the form—

$$h\delta p/p = 2 - Gh^{-\frac{1}{2}} + Ah^{-1} - Bh^{-\frac{3}{2}}$$

is found, which gives expression to the data obtained by extrapolation to 18°.

A new dilution law is proposed of the form—

$$\frac{\alpha^2}{1-\alpha} = K(h-n)^{\frac{1}{2}}.$$

By using this in conjunction with the osmotic relations—

$$\frac{P}{R'T} = \frac{\Delta}{F'} = \frac{\delta p}{p} = \frac{1+\alpha}{h-n},$$

it is possible to evaluate both α and n.

The values of α and n independently obtained from the freezing-point and vapour-pressure data are found to be in good accord, and give values for n at infinite dilution which are in fair accord with those derived from conductivities.

With the more complete series of data for lithium chloride, it is found that a relation exists between α and n which is independent of temperature in the range considered, namely, $n = 38\alpha - 14$.

This enable the conditions of a saturated solution of lithium chloride at 18° to be examined, which shows that the ionisation reaction may be taken to be—

$$2LiClAq + Aq_2 \rightleftharpoons 2LiAq + 2ClAq.$$

This gives, according to the law of mass action, the relation—

$$\frac{\alpha^4}{(1-\alpha)^2} = K'\frac{\beta}{2}(h-n).$$

where β is the weight fraction of the free water, $h-n$, which exists in the form Aq_2, or dihydrol.

This is identical with the assumed dilution law,—

$$\frac{\alpha^2}{1-\alpha} = K(h-n)^{\frac{1}{2}},$$

if—

$$K = \sqrt{K'\beta/2}.$$

It is shown by reference to the figures for α, n, and β that the relation holds, and that K' has the same value both at infinite dilution and in saturated solutions of lithium chloride.

Alternatively, the reaction might be taken to be—

$$2LiClAq + Aq_3 + Aq \rightleftharpoons 2LiAq + 2ClAq + Aq_2,$$

which leads also to the form of the dilution law.

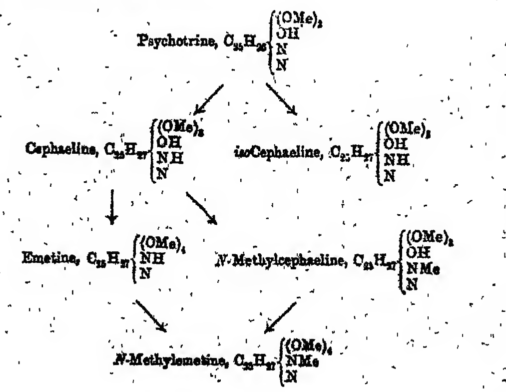
*142. "*The Alkaloids of Ipecacuanha.*" By FRANCIS HOWARD CARR and FRANK LEE PYMAN.

A detailed description was given of an investigation of which a part has previously been reported in a preliminary note (*Proc.*, 1913, xxix., 226). The salts of emitine, cephaeline, and psychotrine have been fully characterised. *Emetine sulphate*, $C_{29}H_{40}O_4N_2,H_2SO_4,7H_2O$, m. p. 205—245° (corr.); *cephaeline hydrobromide*,—

$$C_{28}H_{38}O_4N_2,2HBr,7H_2O.$$

m. p. 266—293° (corr.); *psychotrine nitrate*, $C_{28}H_{36}O_4N_2,2HNO_3,H_2O$, m. p. 184—187° (corr.); *psychotrine sulphate*, $C_{28}H_{36}O_4N_2,H_2SO_4,3H_2O$, m. p. 214—217° (corr.); and *psychotrine hydriodide*, $C_{28}H_{36}O_4N_2,2HI$, m. p. 222° (corr.), are new crystalline salts.

In correction of the previous statement it was shown that emitine and cephaeline are secondary-tertiary bases. Emetine yields a crystalline N-*benzoyl* derivative, $C_{29}H_{39}O_4N_2 \cdot COPh$, m. p. 185—186° (corr.), which is a monacidic tertiary base. Emetine is the O-methyl ether of cephaeline. It gives N-*methylemetine*, an amorphous base yielding crystalline salts, on methylation. Cephaeline yields on methylation a mixture of emetine, N-*methylcephaeline*, m. p. 194—195° (corr.), and N-methylemetine. Psychotrine has the formula $C_{28}H_{36}O_4N_2,4H_2O$, and yields on reduction a mixture of cephaeline and iso*cephaeline* (m. p. 159—160°, corr.). The relation between these alkaloids can be expressed as follows:—



The hydrochlorides obtained by the oxidation of cephaeline with ferric chloride were shown to have the formulæ $C_{18}H_{18}O_3NCl,HCl$ and $C_{20}H_{27}O_3NCl_2,HCl$ respectively.

143. "*The Viscosity of Sugar Solutions.*" By HEBER GREEN.

In a recent paper Powell (*Trans.*, 1914, cv., 1) claims that the relation between the viscosity and concentration of sugar solutions can be expressed by the equation $\eta x = \eta_0 A^x$, where x is the ratio of solute to solvent, and in his discussion of previous work quotes the present author (Green, *Trans.*, 1908, xciii., 2027) as having concluded that the "connection between viscosity and concentration is not accurately expressed, even within the limits of experimental error, by any of the various formulæ that have been suggested."

This is, however, an incomplete quotation, the continuation of the same sentence being to the effect that the best concordance is obtained by the use of an expression of the form $\eta x = \eta_0 A^{v/w}$, where v and w are the volumes of the solute and solvent respectively.

It was shown that the form of this expression supported by Powell merely neglects any possible contraction which may occur when the sucrose dissolves in water, and is not that which gives the nearest approach to accuracy.

The discrepancies between the calculated and observed viscosities are, in any case, far beyond the experimental error of the measurements made by the present author more than five years ago, and he sees no reason to alter the conclusion arrived at then.

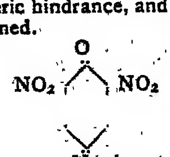
144. "*Compounds of Phenanthraquinone with Metallic Salts.*" By JOSEPH KNOX and HELEN REID INNES.

The following additive compounds of phenanthraquinone and metallic salts have been prepared and analysed: —$C_{14}H_8O_2,ZnBr_2$, $(C_{14}H_8O_2)_2,ZnI_2$, $C_{14}H_8O_2,CdCl_2$, $C_{14}H_8O_2,CdBr_2$, $C_{14}H_8O_2,CdI_2$, $(C_{14}H_8O_2)_2,HgBr_2$.

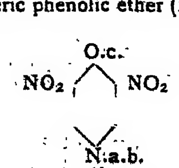
The relative stability of the zinc and cadmium compounds has been determined by finding the concentration of metallic haloid in aqueous solution with which mixtures of phenanthraquinone and the various double compounds are in equilibrium. This equilibrium concentration is a measure of the relative stability. The lower the equilibrium concentration, the greater is the stability of the compound. It has been found that with a given metal the iodide compound is more stable than the bromide, and the bromide than the chloride, whilst the cadmium compounds are more stable than the corresponding zinc compounds. The stability of the compounds therefore increases with diminishing electro-affinity of both the metal and the halogen. The mercuric compounds are more stable than either the zinc or the cadmium compounds, as is shown by their behaviour towards water, and mercury is the metal of weakest electro-affinity of the sub group. The greater complexity of the mercuric compounds compared with the zinc and cadmium compounds and of the zinc iodide compound compared with the zinc chloride and bromide compounds, also illustrates the increasing tendency to complex-formation with diminishing electro-affinity.

145. "*Quinone-ammonium Derivatives.* Part III. *Dihaloid, Monoazo-, Bisazo-, Nitrotriazo-, and Bistriazo-compounds: Attempts to Prepare Derivatives containing an Asymmetric, Quinquivalent Nitrogen Atom.*" By RAPHAEL MELDOLA and WILLIAM FRANCIS HOLLELY.

Taking advantage of the partial and complete reducibility of the nitro-groupe in 2:6-dinitro-4-trimethylammonium-1-benzoquinone (*Trans.*, 1912, ci., 912; 1913, ciii., 177) the authors have prepared a number of new quinone-ammonium derivatives containing naphtholazo- and triazo groups in place of one or both of the original nitro groups. The constitution of the 2:6 dibromo-derivative (*Trans.*, 1913, ciii., 185) has been proved directly by synthesis from 2:6 dibromo-*p*-aminophenol. Systematic attempts to obtain a quinone-ammonium compound of the type (I.) with three dissimilar radicles attached to the nitrogen atom have led to the discovery that this nitrogen atom appears to be incapable of carrying three different radicles when the weight or size of the latter exceeds some limit at present undetermined. If this limit is exceeded, the alkylation apparently takes a normal course, in spite of steric hindrance, and the isomeric phenolic ether (II.) is obtained.



(I.)



(II.)

146. "*The Estimation of Carbon Monoxide.*" By JOSEPH IVON GRAHAM and THOMAS FIELD WINMILL.

As is well known, carbon monoxide is oxidised to carbon dioxide by iodine pentoxide, and various methods of estimating carbon monoxide has been described, based on this reaction. The authors have studied the temperature at which the reaction takes place, and the influence of other gases on its course. A modified form of Haldane's gas-analysis apparatus was described, in which the oxidation may be carried out rapidly, and carbon monoxide estimated with an accuracy of 0·02 per cent.

147. "*Alcoholometry and Rational Fractionation.*" By HENDRIK PIETER BARENDRECHT.

A new distilling apparatus, made from copper, was described, which allows the estimation of alcohol in a fermented liquid, containing between 2 and 3 per cent of alcohol, by concentrating automatically and in one operation all the alcohol in one-twentieth of the original volume. By this arrangement accuracy is easily obtained, even in using an alcoholometer. From very weak solutions, for example, 0·01 per cent, all the alcohol may be distilled off at once in the hundredth-part of a sample of 3 litres.

The construction of this apparatus, as well as of another one (also described), made out of ordinary laboratory glassware, is based on the following principle.

The rectifier, surrounded on the top by an open water-reservoir as a dephlegmator, should have a large volume, filled with a porous substance, to store up and concentrate the volatile liquid, until all of the latter has been boiled out of the sample, and has thereby heated the dephlegmator so far that the liquid can pass to the condenser.

148. "*The Resolution of 5-Nitrohydrindene-2-carboxylic Acid.*" By WILLIAM HOBSON MILLS, HORACE VICTOR PARKER, and ROBERT WILLIAM PROWSE.

With the object of obtaining an optically active benzene derivative in which it should be necessary to take into consideration the relative distribution in space of the substituent groups to account for the optical activity, the authors have prepared 5-nitrohydrindene-2-carboxylic acid, $NO_2 \cdot C_6H_3 {<}{}^{CH_2}_{CH_2}{>} CH \cdot CO_2H$, and have shown that it can be resolved by means of its quinine salt into two antimeric components. Unless the configuration of the nitrophenylene radicle is taken into account, the reason for the molecular asymmetry of this compound does not appear. It is evidently due to the asymmetrical disposition of the nitro-group with respect to the two methylene groups, it being in the meta-position to one and in the para-position to the other.

149. *Researches on Pseudo-bases.*" Part I. "*Some Condensation Reactions of Cotarnine, Hydrastinine, and* iso*Quinoline Methyl Hydroxide.*" By GERTRUDE MAUD ROBINSON and ROBERT ROBINSON.

Cotarnine condenses with 6-nitrohomoveratrole, nitrohomopiperonyl alcohol, or nitropiperonal to yield nitrohomopiperonyl-, nitropiperonylidene-, or nitropiperonoyl-hydrocotarnine respectively. The condensation of *iso*-quinoline methyl hydroxide with 6-nitrohomoveratrole, and of hydrastinine with itself, was also described.

150. *Molecular Conductivities of Iodoanilinesulphonic Acids.*" By MARY BOYLE.

The following monoiodoanilinesulphonic acids have been prepared and the conductivities of their aqueous solutions at 25° determined; 2-, 3-, and 4-iodoaniline-6-sulphonic acids, 2-, 3-, and 4-iodoaniline-5-sulphonic acids, and 2- and 3-iodoaniline-4-sulphonic acids. In all cases where iodine is introduced into an orthoposition to the amino-group, a very considerable increase in molecular conductivity occurs; the increase is much less marked in the case of *m*- and *p*-iodo-substituted acids.

151. "*The Action of Steam on Sodium Chloride.*" (Preliminary Note). By SOLOMON ENGLISH and WILLIAM ERNEST STEPHEN TURNER.

Some years ago Emich (*Ber.*, 1907, xl., 1482) described an experiment in which the production of hydrogen chloride from salt and water was demonstrated by dropping water on sodium chloride heated in a platinum crucible. Another and simpler way of demonstrating the reaction is to drop a solution of salt on the surface of a platinum basin at bright red heat, when not only hydrogen chloride can be detected in the issuing vapour but the residue is distinctly alkaline.

The authors have attempted to determine the extent to which this hydrolytic decomposition occurs by passing steam over sodium chloride in a platinum boat heated to varying temperatures. There is no appreciable action at and below 500°, but it becomes recognisable at 700°, and

increases steadily with rise of temperature, measurements having been made up to 1000°. Sodium chloride possesses an appreciable vapour pressure below its melting-point (800°), and the reaction appears to take place mainly between the salt vapour and steam. In porcelain tubes, however, the amount of hydrogen chloride found exceeds the alkali left as residue, and so far the authors have been unable to trace the reason for the discrepancy. They hope to repeat the determinations in a platinum tube.

152. "*Experiments on the Synthesis of the Benzoterpenes.*" Part I. "*Derivatives of Benzonor-p-Menthane.*" By Francis William Kay and Allan Morton.

An account was given of the synthesis of some representatives of a new class of terpenes, described as the *benzoterpenes*, which have been obtained from the various derivatives of α-naphthoic acid with the aid of Grignard's reagent.

PHYSICAL SOCIETY.

Ordinary Meeting, May 22, 1914.

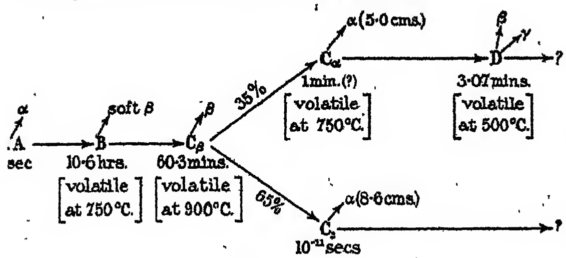
Dr. A. Russell, Vice-President, in the Chair.

A paper entitled "*Volatility of Thorium Active Deposit,*" by T. Barratt, B.Sc., and A. B. Wood, M.Sc., was read by the former.

On heating thorium active deposit to various accurately measured temperatures up to about 1250° C. it is found that B and C each commence to volatilise at 750° C., but the volatilisation is not complete until 1200° C. is reached, the measurements being made by an α-ray electroscope. The C curve is peculiar, being similar to two of the B curves placed end to end, the inflexion occurring between 750° C. and 900° C., where about 35 per cent of the α-activity is removed.

When measured by β radiation, C is not volatile until a temperature of 900° C. is reached. D commences to volatilise at 500° C.

In explanation of these results it is assumed that the part of C which produces β-rays, viz., C_β, is a separate product, which is not so readily volatile as C_α, and the following scheme of disintegration is suggested:—



Discussion.

Dr. R. S. Willows congratulated the authors on their able treatment of the subject. The suggested scheme met most of the requirements of the case and was not in contradiction with any of the other known properties of the thorium series. He hoped the authors would extend their work to other radio-active series.

Dr. S. Russ drew attention to the apparent lack of parallelism between the characteristics of the thorium and radium series. The volatility of thorium B appeared to be not very different from that of thorium C, whereas in the radium series, radium B is the most, and radium C the least, volatile of the series. Again, the authors concluded that there was no appreciable difference in the volatility of the thorium active deposit from a quartz or a platinum surface, whereas there was an appreciable difference in the case of the radium active deposit, as Dr. Makower had shown.

Mr. D. Owen observed that one of the products was stated to have a period of 10^{-11} second. He thought it hardly possible to catch a product which only lived for that time.

Mr. Barratt said that only two surfaces were used, quartz and platinum, on account of the high temperature to which they had to be subjected. In these cases there had certainly been no difference. When different acids were used, considerable differences were observed in the temperature of volatilisation. The period, 10^{-11} second, assigned to ThC_2 was simply in order to fit the Geiger-Nuttall relation. The curve connecting log (γ) and log (Range) is a straight line, and the period 10^{-11} second was necessary to make the product fit the curve.

A paper entitled "*The Passage of α-Particles through Photographic Films,*" by H. P. Walmsley, M.Sc., and W. Makower, M.A., D.Sc., was read, in the absence of the authors, by Dr. S. Russ.

It has been shown by Kinoshita that when an α-particle strikes a grain of silver halide, that grain is subsequently capable of photographic development. It therefore seemed probable that the path of an α-particle projected tangentially to a photographic film should, after development, be visible under a microscope. This was shown to be the case, and micro-photographs showing the tracks of α particles through a photographic plate have been obtained. The effect of "scattering" of α-particles can also be seen in the photographs, and this method may prove of use in studying the scattering of α-particles by heavy atoms such as silver. This method of studying the path of an α-particle possesses the advantage of great simplicity.

A paper "*On a Null Method of Testing Vibration Galvanometers*" was read by S. Butterworth, M.Sc.

The methods usually employed in the determination of the constants of a vibration galvanometer involve the measurement of a deflection under three different conditions. Two of these deflections can only be obtained very approximately.

By extending the theory of the vibration galvanometer it is shown how the constants may be determined by methods which involve only the measurement of one deflection. The remaining measurements are carried out on an alternating-current bridge, and the results obtained are practically independent of the wave-form of the source.

The principle of the method depends on the fact that a vibration galvanometer behaves as a parallel combination of a conductance, a capacity and an inductance, in series with a resistance. It is shown how to balance such a combination, and the method is illustrated experimentally. The constants of various galvanometers are quoted in order to show the applicability of the method. Other uses of the bridge are suggested.

Discussion.

Mr. A. Campbell remarked that it was most interesting to find that the electrical behaviour of a circuit capable of dynamical resonance could be imitated exactly by putting in parallel a resistance, a condenser, and an inductance. It was a pity that this combination could not be realised in practice since the inductance must have zero resistance. However, Mr. Butterworth got over the difficulty by his special form of bridge. The limitations of this bridge somewhat lessened the range of application to practical cases, and he hoped that the author would be able to modify the bridge so as to remove these limitations.

Mr. D. Owen stated that he had found no difficulty in maintaining the frequency of the source sufficiently steady to maintain the voltage sensitivity of a vibration galvanometer constant within 1 or 2 per cent for a considerable time. The author's analysis of the vibrating coil was very ingenious, but one would like to know whether sensitivities calculated by his rather complex bridge agreed with those obtained by the usual direct method.

Dr. R. S. Willows asked whether the method could be used to find the dielectric constant of a slightly conducting liquid; if so, was it sensitive enough to be practically useful and did the largeness of the required inductance again limit its applicability.

Mr. Butterworth, in reply, stated that the method would apply to any vibrating system provided that the conditions mentioned in the paper could be satisfied. It was true, as Mr. Owen had pointed out, that the *voltage* sensitivity of certain galvanometers could be determined very precisely. This held in the case of instruments capable of developing a high back E.M.F. The reduction of current at resonance would then prevent any considerable rise in the vibration in spite of the large increase in *current* sensitivity. The application of the method to the measurement of small capacities required investigation.

"*Experiments with an Incandescent Lamp*" were described and exhibited by Mr. C. W. S. Crawley and Dr. S. W. J. Smith.

The first of these experiments was due to Mr. Addenbrooke, who, using a 100-volt lamp filled with paraffin oil (after removing the tip) as a convenient high resistance in a 200-volt circuit, noticed that some of the many bubbles forming on the filament behaved in a curious way. Instead of rising at once to the surface from the point at which they formed they ran down the legs of the filament, against gravity, and then escaped at the leading-in wires.

Dr. Smith, led to repeat this experiment by Mr. Crawley, discovered another, more striking, phenomenon. Placing the 100 volt lamp in a 100-volt circuit in series with a variable resistance (conveniently a water-trough) it was found possible, by momentarily cutting out most of the resistance, to obtain a single bubble upon the wire. The behaviour of such a bubble is very interesting to watch. Instead of escaping at either terminal, as in Mr. Addenbrooke's experiment, it travels backwards and forwards between the two, "looping the loops" of the filament in a fascinating way during every journey.

The peculiarities of this phenomenon, which can be obtained with either direct or alternating supply, have been analysed by examining the size and motion of the bubble under various conditions, and also by using filaments of different materials and liquids of different boiling-points.

It was shown, from the experiments, that a rapid fall of temperature from the wire through the liquid, in the region through which the bubble moves, is an essential condition of the phenomenon, and also, from theoretical considerations, how this condition can be used to explain why the bubble moves in the manner described.

Mr. Crawley pointed out, in connection with the first experiment, that the lamp proved most satisfactory, being able not only to absorb more power than with a vacuum, but also to stand momentary overload much better.

NOTICES OF BOOKS.

Nucleic Acids, their Chemical Properties and Physiological Conduct. By Walter Jones, Ph.D. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1914.

This monograph discusses with great completeness a very important branch of biochemistry, and it will be the more welcome because no treatise devoted exclusively to the subject has appeared before. The author is well qualified to supply the want, having done a considerable amount of valuable original work on the nucleic acids and allied substances, and he displays a sound critical judgment in his estimation of the value of the researches and deductions of other investigators. It is perhaps no disadvantage that his views are generally very definitely expressed, and that he shows no tendency to halt between two opinions. In the first part the chemical properties and the structure of the thymus and yeast nucleic acids are exhaustively studied, and in Part II. their physiological conduct is treated in detail. An appendix describes some practical work, such as the preparation of the nucleic acids and the analytical chemistry of the purine and pyrimidine derivatives.

The Simpler Natural Bases. By George Barger, M.A., D.Sc. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1914.

This monograph deals with the basic substances found in animals and plants which are of general biological interest. A more or less arbitrary choice of material has been made, and certain groups of substances, such as the purine bases, are entirely omitted. On the other hand, those which are included are given fairly full treatment, their physiological action as well as their chemical properties and constitution being adequately discussed. The practical methods of isolating and studying the bases which were employed by their discoverers and investigators are described, and the student will be able to gather from the monograph many suggestions as to fruitful research work.

Alloys and their Industrial Applications. By Edward F. Law. Second Edition. London: Charles Griffin and Co., Ltd. 1914.

In the second edition of this book the results of recent investigations are incorporated, and a thoroughly practical account is given of the properties and industrial applications of alloys. Methods of investigating alloys are clearly described, the details being sufficiently full for the purposes of students of metallurgy. The purely scientific research work which has been published recently in great abundance is not included, the book being intended chiefly for the practical man. Specially important alloys, such as brasses and bronzes and the iron alloys, are treated very fully, and some interesting new illustrations have been added to the second edition.

Metropolitan Water Supply. Extract from the Annual Report of the Local Government Board for 1912—1913. London: Printed under the Authority of His Majesty's Stationery Office by Darling and Son, Ltd. 1914.

The results of the periodical inspections made by Mr. C. Perrin as Water Examiner under the Metropolis Water Act are contained in this report, and some account is given of the works in progress for the extension and improvement of the Metropolitan Water Supply. Dr. A. C. Houston's new method of using lime in the softening, purification, and sterilisation of water ("excess lime method") is also described. Many experiments have been carried out in investigating this method, and its advantages and disadvantages are very fully discussed. There appears to be no doubt that it enables flood water to be safely and speedily used, and that it absolutely eliminates danger from epidemic water-borne diseases.

The Utilisation of Solar Energy. By A. S. E. Ackermann, B.Sc.(Engineering), A.C.G.I., M.Cons.E., Assoc. M. Inst.C.E. London: The Society of Engineers (Incorporated). 1914.

This pamphlet contains a paper which was read before the Society of Engineers in April last, and which dealt with a subject of the highest importance both scientifically and commercially. It is probably not within the knowledge of the average man that water can be made to boil by the unconcentrated rays of the sun, and although a good deal is said of the necessity for husbanding the earth's store of fuel, it is perhaps hardly generally realised that by the end of the present century the problem of supplying mills and factories with fuel will have become acute in America and more so in Europe. This being so, these accounts of the official tests of sun-power plants are of peculiar interest. The author describes the early types of the Shuman plant, in the first of which no means of concentrating the sun's rays were employed; afterwards in the 1911 form of apparatus plane glass mirrors were used to concentrate the rays, while finally in the 1913 type of absorber parabolic mirrors are used (Shuman-Boys absorber). The official tests carried out with this latest form of apparatus are described in detail, and the results are remarkable enough to deserve the very serious attention of engineers. The

author writes in a temperate spirit, and the pamphlet is an important addition to our knowledge of a new means of power production.

First Report of the Departmental Committee on the Heat Test as Applied to Explosives. London: Printed under the Authority of His Majesty's Stationery Office by Darling and Son, Ltd. 1914.

This report gives the details of the Committee's work in connection with the standardisation of the apparatus and materials used in the Abel Heat Test for explosives. The preparation of the sample to be tested and the application of the test are described in full. All the apparatus is illustrated by diagrams drawn to scale, and the report contains a short account of the visit of the Committee to the "Centralstelle für Wissenschaftlich-technische Untersuchungen" at Neubabelsberg, when Prof. Will stated his views upon the question of stability tests for propulsive explosives.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clviii., No. 17, April 27, 1914.

Action of Chloroform on Metallic Sulphates. Preparation of Anhydrous Chlorides.—Auguste Conduché.—Metallic sulphates are readily converted into anhydrous chlorides by vapour of chloroform at comparatively low temperatures. The following are the temperatures at which the reaction begins:—$CuSO_4$, 250°; $NiSO_4$, 300°; $FeSO_4$, 300°; $MnSO_4$, 350°; $PbSO_4$, 350°; $Al_2(SO_4)_3$, 400°; $MnSO_4$, 450°; $BaSO_4$, 500°; $CaSO_4$, 500°; Na_2SO_4, >500°. At these temperatures, however, the transformation is slow and incomplete, and practically a higher temperature is necessary. At 400—500°, however, the chloroform itself decomposes, giving deposits of carbon, so that pure chlorides can be obtained only at low temperatures. In the case of copper the method is the best to employ for the preparation of the chloride.

Alkaloid obtained from Galega officinalis.—Georges Tanret.—*Galega officinalis* is a herbaceous leguminous plant which is much cultivated in France. The author has obtained from its seeds a new alkaloid which he calls galegine. It fuses at 60° to 65°; it has no rotatory power, and is very soluble in water and absolute alcohol. Its formula is $C_6H_{12}N_3$, and the composition of its sulphate and of other salts shows that it is a monovalent base.

Preparation of Pure Butine.—M. Picon.—Pure butine can be prepared by the action of ethyl iodide upon monosodium acetylene. It is a colourless gas with an odour resembling that of pure carbon disulphide. The author finds that it boils at 8·3° under normal pressure, this being a much lower boiling-point than that previously ascribed to it. The gas is absorbed by all the reagents for true acetylenic hydrocarbons; it give a white precipitate with aqueous or alcoholic alkaline potassium iodomercurate, a white precipitate with alcoholic or ammoniacal silver nitrate, and a pale yellow precipitate with ammoniacal cuprous chloride.

Derivatives of 2, 6-Octadiine-1, 8-diol.—M. Lespieau.—The glycol function of—

$$CH_2OH.C{\equiv}C.CH_2.CH_2.C{\equiv}C.CH_2OH$$

is confirmed by the existence of a diacetine, and its unsaturated nature is proved by the fact that it fixes bromine and iodine. The product of hydrogenation is the saturated linear biprimary glycol $C_8H_{18}O_2$, which has been obtained by the hydrogenation of ethyl suberate.

MISCELLANEOUS.

Royal Institution.—A General Meeting of the Members of the Royal Institution was held on the 8th inst., The Duke of Northumberland, President, in the Chair. Mr. H. B. Hans Hamilton, Sir William H. Lever, Bart., Mr. Percy St. C. Matthey, J.P., Mr. H. W. P. Matthey, Miss Matthey, Mr. J. F. C. Snell, and Mr. T. J. Taylor were elected Members. The Chairman reported the decease of Sir Francis Laking and Sir Joseph Swan, Members of the Institution, and Resolutions of Condolence with the families were passed. The Secretary announced that His Grace the President had nominated the following gentlemen as Vice Presidents for the ensuing year:—Lord Blyth, Mr. J. H. Balfour-Browne, Mr. Charles Hawksley, Dr. Donald Hood, Lord Moulton, Mr. E. Pollock, Sir James Crichton-Brown (Treasurer), and Mr. Alexander Siemens (Secretary).

The Wellcome Historical Medical Museum.—The Historical Medical Museum, which was founded by Mr. Henry S. Wellcome in connection with the Seventeenth International Congress of Medicine, was re-opened on May 28th as a permanent institution in London. It is now known as the "Wellcome Historical Medical Museum," and is open daily from 10 a.m. to 6 p.m., closing at 1 p. m. on Saturday; entrance 54a, Wigmore Street, Cavendish Square, W. Since closing last October the collections in the Museum have been considerably augmented and entirely rearranged. Many objects of importance and interest have been added, which it is hoped will increase the usefulness of the Museum to those interested in the History of Medicine. Members of the medical and kindred professions are admitted on presenting their visiting cards. Tickets of admission may be obtained by others interested in the History of Medicine on application to the Curator, accompanied by an introduction from a registered medical practitioner. Ladies will be admitted *only* if accompanied by a qualified medical man.

MEETINGS FOR THE WEEK.

Thursday, 18th.—Royal Society, (1) "Trypanosome Diseases of Domestic Animals in Nyasaland, *Trypanosoma caprae* (Kleine)—Part III., Development in *Glossina morsitans*; (2) Trypanosomes found in Wild *Glossina morsitans* and Wild Game in the 'Fly-belt' of the Upper Shire Valley; (3) Food of *Glossina morsitans*; (4) Infectivity of *Glossina morsitans* in Nyasaland during 1912 and 1913," by Surg.-Gen. Sir D. Bruce, Major A. E. Hamerton, Capt. D. P. Watson, and Lady Bruce. "Relation between the Thymus and the Generative Organs, and on the Influence of these Organs upon Growth," by E. T. Halnan and F. H. A. Marshall (with a note by G. U. Yule). "Vapour-pressure Hypothesis of Contraction of Striated Muscle," by H. E. Roaf. "Validity of the Microchemical Test for the Oxygen Place in Tissues," by A. N. Drury. "Man's Mechanical Efficiency," by J. S. Macdonald. "Colouring Matters in the Compound Ascidian *Diazona violacea*," by A. Holt.

— Chemical, 8.30. "Nitrogenous Constituents of Hops," by A. Chaston Chapman. "The Isomerism of the Oximes—Part IV., Constitution of the N-methyl Ethers of the Aldoximes and the Absorption Spectra of Oximes, their Sodium Salts and Methyl Ethers, by O. L. Brady. "Wet Oxidation of Metals—Part III., The Corrosion of Lead," by B. Lambert and H. E. Cullis. "Studies in the Camphane Series—Part XXXV., Isomeric Hydrazoximes of Camphorquinone and some Derivatives of Aminocamphor," by M. O. Forster and E. Kunz. "Velocities of Combination of Sodium Phenolates with Olefine Oxides," by D. R. Boyd and E. R. Marle. "Colouring Matters contained as Glucoside in the Flowers of some Indian Plants," by A. G. Perkin and I. Shurlman. "A New Chlorocamphor," by T. M. Lowry and V. Steele. "Ideal Refractivities of Gases," by W. J. Jones and J. R. Partington. "Purification and Physical Properties of α-Bromonaphthalene," and "Determination of Water in Alcohol-water Mixtures by the Clouding Points of Mixtures with α-Bromonaphthalene," by M. Jones and A. Lapworth.

THE CHEMICAL NEWS.

VOL. CIX., No. 2847.

THE PREPARATION OF EYE-PRESERVING GLASS FOR SPECTACLES.*

By Sir WILLIAM CROOKES, O.M., F.R.S.

(Continued from p. 280).

Copper.

COPPER by itself as a constituent of glass is not of much advantage. It colours the glass blue, has not much action on the ultra-violet rays, but cuts off three-fourths of the heat rays. It forms a useful addition to other colouring agents in tending to neutralise those of the orange-yellow colour.

Iron (FeO).

Iron is introduced into the glass as ferrous sulphate, care being taken to avoid all oxidising agents. The fused mass is stirred with a carbon rod, and a little powdered charcoal added to the melt in the crucible. In quantities from 1 to 2·5 per cent the obstruction to heat radiation is great, and increases with the quantity of metal present. One per cent of iron cuts off about 65 per cent of the heat, and 2·3 per cent cuts off about 89 per cent. The action on the ultra-violet end is but slight, the photographs extending to λ 3467 with the lowest amount of iron, and to λ 3560 with the largest amount experimented with. The light transmitted by the 2 mm. plate is 71 per cent with the least amount of iron and 50 per cent with the largest amount. The colour of the glass is greenish blue. Iron in the ferrous state, therefore, will prove useful on account of its communicating adiathermic property to the glass.

Iron (Fe_2O_3).

In this state of oxidation iron glass cuts off ultra-violet light to a limited extent. When small proportions only are present, such as 0·25 per cent, the rays are transmitted from λ 3500 (far in the ultra-violet), and it is only when the amount of iron in the per state rises to about 2 per cent that the glass becomes opaque to the rays near λ 4000 (about the limit of visibility in the violet). A glass of this composition cuts off about 63 per cent of the total heat. The colour is almost pure yellow. The glass transmits about 75 per cent of the incident light. Iron in the per state, therefore, is another metal useful in combination.

Lead.

A plate 2 mm. thick was cut from a block of Faraday's "heavy glass" (boro-silicate of lead) prepared by himself, and tested as a sample of lead glass. It is practically colourless and transparent, and is opaque to the ultra-violet above λ 3800. Its action on the heat rays is slight, only cutting off about 38·5 per cent.

Manganese.

Glass containing manganese is of a reddish purple colour. In respect to obstruction to the ultra-violet and heat rays manganese has no special action. It has, however, been experimented with to obtain a neutral coloured glass by adding it to glass containing a greenish colouring agent.

Neodymium and Praseodymium.

These two bodies would be useful in the quest for a suitable glass were they to be obtained at a price which would not be prohibitive. In aqueous solutions praseodymium salts are greenish yellow, and those of neodymium are of a violet-rose colour. Mixed together in the proportion of five parts of praseodymium to one of neodymium the mixture is of a neutral grey. In solid solution in glass the colours are—praseodymium greenish yellow, and neodymium lilac. Melted together in glass in the same proportion as in aqueous solution, the resulting colour is also neutral grey. In this respect these two elements differ from nickel and cobalt, inasmuch as the colours remain constant either in aqueous solution or melted in glass, and the proportion required to obtain neutrality of tint appears to be the same in each case.

Uranium.

Glasses were prepared containing from half a per cent of uranium to over 4 per cent. The colour of the glasses with smallest quantity of metal is very faint brown, and with the highest proportion it is yellowish brown. The opacity for ultra-violet light increases as the glass is richer in metal, the one with about 4 per cent uranium being opaque to the indigo and violet down to the blue. The heat absorbed at most is about 55 per cent. These results show that uranium is a metal likely to be useful in combination.

Composition of Glasses Specially Selected for Practical Use.

Whilst bearing in mind that the chief object of this research is to find a glass that will cut off as much as possible of the heat radiation, I have also attacked the problem from the ultra-violet and the transparency points of view. Taking each of these desiderata by itself I have succeeded in preparing glasses which cut off over 90 per cent of heat radiation, which are opaque to the invisible ultra-violet rays, and are sufficiently free from colour to be scarcely noticeable when used as spectacles. But I have not been able to combine in one specimen of glass these three desiderata in the highest degree. The ideal glass which will transmit all the colours of the spectrum cutting off the invisible rays at each end, is still to be discovered.

As far as transparency, however, is concerned it will not be an unmixed advantage for the sought-for glass to be quite clear and colourless. The glare of a strong light on white cliffs, expanses of snow, electric light, &c., is known to be injurious to the eye, and therefore a tinted glass combining good obstruction to the heat radiation and ultra-violet rays is the best to aim for.

Grey or neutral tints are the most pleasant to wear. They do not appreciably alter the natural colours of objects, and are a great relief to the eye. Many glasses are met with in commerce of different colours which are found by experience to suit the public demand for tinted spectacles. They are of various tints of yellow, green, blue, and neutral, and therefore I do not think it will be wrong to select the tints of my glasses, suitable in other respects, no darker than those which appear to suit the public taste.

As a basis for the preparation of the coloured glasses, Mr. Powell prepared for me a quantity of hard soda-flux mixture of the following composition:—

Sand	61·00
Sodium carbonate, anhydrous	25·50
Sodium nitrate, re-crystallised	5·00
Calcium carbonate, precipitated	7·20
Borax	0·75
Arsenic trioxide	0·55
	100·00

This mixture whilst melting loses about 25 per cent in weight. When first melted, it is colourless; on second melting it acquires the usual faint greenish tint of soda-lime glass. The contents of a large potful of the melted flux was poured into cold water. The broken-up mass was sent to my laboratory and has been used in the preparation of the test glasses. The object of pouring the molten flux into water is to break it up and render it easy to powder for convenience of adding other ingredients. In this state I call it "Fused Soda Flux."

* Read before the Royal Society, November 13, 1913. From the *Philosophical Transactions of the Royal Society*, Series A, vol. ccxiv., pp. 1—25.

Sometimes it is found advisable to use the flux in its raw state without previous melting, and when working upon the large scale this is the best plan. I then call it "Raw Soda Flux."

Without counting numerous preliminary experiments, I have made and fully tested over 300 tinted glasses, the quantitative composition of each being known. From these glasses I have selected a certain number which possess valuable qualities in respect of athermancy, adiactinity, and transparency.

I will now give the composition of these glasses, and the special properties in respect to the desired results.

Glass 150.

Fused soda flux	90·00
Cerium borate	8·13
Nickel sulphate, crystallised	0·07
Uranoso-uranic oxide	1·80
	100·00

In Glass 150 a small amount of nickel has been added to the cerium and uranium. The colour is pale yellow, and it is opaque to ultra-violet radiation, the limit being λ 3613. It cuts of 37 per cent of the heat radiation and transmits 73 per cent of the incident light. The tintometer numbers are:—Red, 4·0; yellow, 3·5; blue, 0·5.

Glass 158.

Fused soda flux	89·75
Cerium borate	8·18
Ferroso-ferric oxide..	2·03
Chromic oxide	0·09
	100·00

This glass is pale greenish yellow. It is quite opaque to all the ultra-violet rays, the limit being λ 3700. It cuts off 63 per cent of heat radiation, and transmits 54 per cent of the light.

The glass has a pale greenish yellow colour. Its tintometer numbers are:—Yellow, 2·75; blue, 3·5.

Glass 165.

Raw soda flux	87·56
Cerium borate	8·00
Ferrous sulphate, crystallised ..	3·00
Uranic oxide	0·55
Nickel oxide	0·09
Chromic oxide	0·80
	100·00

This glass cuts off practically all the ultra-violet rays shorter than λ 3680, and 38 per cent of the heat radiation. It transmits 48 per cent of the light. Its colour is a pale yellowish green. Its tintometer numbers are:—Yellow, 4·0; blue, 2·50.

Glass 187.

This glass and the next are both cerium glasses. No. 187 is composed of:—

Fused soda flux	83·0
Cerium nitrate, crystallised	17·0
	100·0

The heat rays cut off by this glass are only 27 per cent, but its other qualifications are important. It is practically opaque to ultra-violet radiation, the limit being λ 3650, and it transmits 99 per cent of the light.

In the tintometer and opacity meter no colour or want of transparency can be detected, although against white paper in a good light a faint tinge of yellow is perceptible.

Glass 197.

Fused soda flux	79·00
Cerium nitrate, crystallised	20·50
Nickel sulphate, crystallised	0·30
Cobalt sulphate, crystallised	0·05
Uranoso-uranic oxide	0·15
	100·00

Nickel and cobalt are here mixed in the proportion to make a neutral tinted glass, the other ingredients only slightly modifying the colour. The colour is a pale neutral. It is opaque to ultra-violet rays of shorter wave-length than λ 3700, and cuts off 41 per cent of the heat rays. It is transparent to 45 per cent of the incident light. The numbers in the tintometer are:—Red, 2·00; yellow, 3·00; blue, 5·50.

Glass 202.

I have obtained a neutral tinted glass by neutralising the orange-yellow colour communicated to glass by iron in the ferric state, by adding to it a little cobalt, which colours it blue. The composition is:—

Soda flux	95·15
Fe_2O_3	4·75
$CoSO_4,7H_2O$	0·10
	100·00

The resulting glass is opaque to ultra-violet of shorter wave-length than λ 3830, it cuts off 83 per cent of the heat radiation, and transmits 25 per cent of light. The tintometer numbers are:—Yellow, 2·5; blue, 5·5.

Glass 210.

Fused soda flux	89·0
Ferrous sulphate, crystallised ..	8·9
Chromic oxide	1·3
Carbon, in fine powder	0·8
	100·0

Glass 210 is of a bluish green colour, the blue colour communicated by the ferrous oxide making the colour of the chromium not so pure a green. It cuts off all ultra-violet rays of shorter wave-length than λ 3620. It obstructs 87 per cent of the heat radiation, and transmits 30 per cent of light. The tintometer numbers are:—Yellow, 2·0; blue, 16·0.

Glass 217.

A further attempt was now made to get the iron in the ferrous state, and a glass was prepared of the following composition:—

Fused soda flux	96·80
Ferroso-ferric oxide..	2·85
Carbon	0·35
	100·00

A few percentages of finely powdered carbon are added to this mixture before fusion to keep the iron in the proto-state. Any excess of carbon rises to the top of the fused mass and prevents oxidation of the iron. This glass is of a pale blue colour, and cuts off the ultra-violet rays shorter than λ 3550. It cuts off 96 per cent of the heat radiation, and transmits 40 per cent of light. Spectacles made of this glass are very pleasant. The glass is bluish with a tinge of green. In the tintometer the numbers are:—Yellow, 2·0; blue, 8·0.

Glass 221.

Fused soda flux	80·0
Cerium nitrate, crystallised	13·4
Uranoso-uranic oxide	6·6
	100·0

In this glass the action of uranium on the ultra-violet rays is added to that of cerium. The colour is faint yellow. It practically cuts off all the ultra-violet radiations, the limit being λ 3685, and it also cuts off 39 per cent of the heat rays. Its transparency is 60 per cent. In the tintometer the number is:—Yellow, 8·0.

Glass 238.

Raw soda flux	77·0
Cerium nitrate, crystallised	23·0
	100·0

Glass 238 is similar in composition to Glass 187, but it contains more cerium. Like 187 it is practically opaque to ultra-violet light, the limit being about λ 3610, the injurious rays being beyond this wave-length. It cuts off 34 per cent of the heat, and transmits 71 per cent of the luminous rays. In the tintometer the numbers are:—Red, 0·375; yellow, 0·375; blue, 1·500.

(To be continued).

DIFFUSION AND MEMBRANE POTENTIALS.*

By E. B. R. PRIDEAUX, M.A., D.Sc.

WHEN two solutions of the same salt of different concentrations, or of different salts, are separated by a porous diaphragm, there is generally an e.m.f. set up at this which differs in magnitude from the diffusion e.m.f. at the junction of the same two solutions without any separate membrane.

In considering the possible cause of this potential, it would seem to be important to emphasise the distinction between those membranes which are capable of furnishing ions of the electrolyte and those which are not.

There is an essential difference between chemical precipitation membranes, such as those of copper ferrocyanide, and organic tissue membranes, such as parchment, collodion, or gelatin. The former kind may, as Beutner has pointed out, act to some extent like the AgCl and other electrolytically conducting solids investigated by Haber and Beutner; they form a reserve of ions and behave to some extent like metallic electrodes. Beutner, for example, observed an e.m.f. of 0·115 volt which remained steady for ten minutes in the combination:—

$$K_4Fe(CN)_6 \mid Cu_2Fe(CN)_6 \mid CuSO_4.$$

He supposes that this e.m.f. is due to the concentration fall between K· in the $K_4Fe(CN)_6$ and the small K· present in the $CuSO_4$. There is a small amount of double ferrocyanide of K and Cu in the membrane which is reversible with respect to K ions. If the $CuSO_4$ side is stiffened with gelatin, so as to prevent the diffusion into the body of solution of those K ions which are continually being produced on this side, then the e.m.f. drops to 0·003—0·010 volt.

This valuable hint as to the nature of $Cu_2Fe(CN)_6$ membrane was not available when the author commenced a series of researches which were devised to ascertain to what extent such a membrane hindered the motion of the ions of a salt—sodium benzoate—which as a whole diffuses through with great slowness. Although potentials were obtained with this solution, which, unlike those observed by Beutner, remained constant over long periods and also gave a regular alteration of e.m.f. with concentration gradient, yet the substitution of another membrane sometimes gave results differing from the former by far greater amounts than could be accounted for by experimental error. The anomaly could only be accounted for by the superposition of irreversible effects and effects of reactions with materials of the membrane, upon those due to the selective hindrances of ionic diffusion.

It was decided, therefore, to investigate those simpler cases in which the latter cause alone was likely to be operative.

This simplification is to be expected in the case of cellulose or other organic tissue membranes, which have a particular importance to physiological chemistry on account of their similarity to animal and vegetable membranes.

The e.m.f.'s observed in muscles, nerves, &c., have been assigned by Ostwald (*Zeit. Phys. Chem.*, 1890, vi., 71) to a selective permeability of ions. The effect may be divided into two parts;—

1. Hindrance of ionic motion due to the nature of the solid membrane.
2. Hindrance of ionic motion due to the sugars, starches, &c., which alter the properties of the solution within the membrane as compared with the solution outside.

The following investigation obviously deals with the first of these effects.

The simple theory of an e.m.f. due to selective permeability of two ions through a membrane is of course merely an extension of the theory of diffusion potential. A diffusion e.m.f. is found for the membrane which is supposed to be due to the difference in the relative ionic mobilities in that medium as compared with the ionic mobilities in the solution. Little experimental work appears to have been done with the following definite objects:—

1. Ascertaining over what range of concentration, if any, a constant transport number of the anion in a membrane could be defined.
2. How far such transport number differs from that in the solution.

To a research on the diffusion potential due to sharp and mixed surfaces of separation Cumming (*Trans. Far. Soc.*, 1913, vii., 5) has added a note on the use of membranes. The symmetrical combination—

$$(1)\ HgHgClN{\cdot}KCl \underset{a}{\mid} \text{connecting solution} \underset{b}{\mid} N{\cdot}KClHgClHg(2)$$

was rendered unsymmetrical by the interposition of a membrane at *a* while at *b* the liquids were mixed. If the membrane was parchment the electrode (1) on the side of the membrane was + to the other to the extent of 3 mv. when the connecting solution was HCl, and (1) was about 6 mv. − to (2) when the connecting solution was NaOH. With LiCl (1) was + to (2) by 0·6 mv.

These results on the whole point to a strengthening of the diffusion potential by the membrane, *i.e.*, to an exaggeration of the differences between the anion and cation mobilities. The difference between membrane and diffusion potentials gradually disappeared with time, indicating perhaps a gradual removal of the mixed layer from the membrane by diffusion.

In the following series of measurements parchment paper was chosen as the membrane material on account of its wide employment in chemical and biological researches, which gives a value to any additional knowledge of its properties.

A salt was required which should, as a whole, diffuse only slowly through the membrane, and which should not furnish any appreciable amount of H′ or OH′ by hydrolysis. Sodium benzoate proved suitable in these respects. It was considered important to use a binary salt in order to reduce the uncertainty in the calculation of ionic concentrations.

The amount of sodium benzoate diffusing from a N/5 solution through parchment into pure water was found to be small. It was not sufficient to influence the e.m.f. in a day, if the weaker side was at least N/10. When there was N/2 solution on one side and N/100 upon the other a slow fall of e.m.f. with time was observed. In such cases the more dilute or both solutions were analysed immediately after reading the e.m.f.

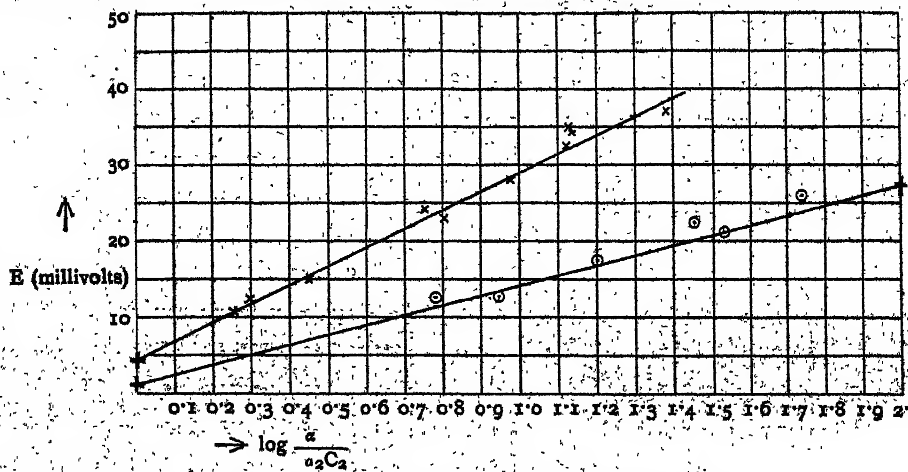
The combination actually used was—

$$HgHgClN{\cdot}KCl \left| \begin{matrix} NaB \\ C_1 \end{matrix} \overset{\text{membrane}}{} \begin{matrix} NaB \\ C_2 \end{matrix} \right. N{\cdot}KClHgClHg.$$

The temperature variation of the membrane e.m.f. itself for variations of a few degrees in the neighbourhood of 18° was shown to be unimportant, that in the calomel electrodes is, of course, eliminated by their opposition. The quality in temperature of the two electrodes was in most cases checked by a measurement of the one against the other when they were connected by N·KCl.

The diffusion potentials of N·KCl against C_6H_5COONa at concentrations C_1 and C_2 was eliminated by a concentrated solution of potassium chloride (3·5 N). At present

* A paper read before the Faraday Society, April 22, 1914.



Electromotive Force and Ionic Concentration.

⊙ ⊙ Diffusion e.m.f. × × Membrane e.m.f. + + Calculated from equation.

it cannot be stated certainly that the saturated KCl eliminated the diffusion e.m.f. at the junctions—

$$N{\cdot}KCl \mid \underset{C_1}{C_6H_5COONa} \qquad N{\cdot}KCl \mid \underset{C_2}{C_6H_5COONa}$$

but the probability that these were either eliminated or brought to very low values, and their difference therefore almost eliminated, is strengthened by the result of the measurements of the diffusion e.m.f. of C_6H_5COONa C_1 against C_2.

The membrane was secured by rubber rings and metal clamps between two flanged glass tubes held horizontally, closed at the ends by stoppers containing glass tubes bent at right angles to make connection with the calomel electrodes. The e.m.f. became constant as soon as the combination was set up, whereas that of the copper ferrocyanide previously investigated often required half-an-hour or more to attain a steady value. The more dilute solution was in all cases positive.

Ionic Concentrations.

These were calculated from the molecular conductivities in the usual manner. The data in Kohlrausch and Holborn's "Leitvermogen" were supplemented by determination of conductivities from 0·1 N to 1 N.

The values at 25° are as follows:—

C =	1·0	0·5	0·2	0·1	0·05	0·02	0·01
λ =	42·2	52·6	62·0	67·2	70·4	74·5	76·5

$\underbrace{70{\cdot}4 \quad 74{\cdot}5 \quad 76{\cdot}5}_{\text{interpolated.}}$

The values of [Na·] or ac as tabulated below were plotted against C and the values ac in the table have been read off from this.

C =	0·01	0·02	0·05	0·10	0·20	0·50	1·00
ac =	0·0086	0·0167	0·0395	0·0755	0·139	0·295	0·472

Diffusion Potentials.

The transport numbers of Na· and C_6H_5COO' in aqueous solution with which were to be compared those in the membrane may in the first place be determined from the data collected by Bredig (*Zeit. Phys. Chem.*, 1894, xiii., 191). From the ionic mobilities at high dilution of Na· = 49·2 and C_6H_5COO' = 31·2, the transport number of the anion (n_A) is 0·388 and $1 - 2n_A$ is 0·224. It was desirable to supplement this by a determination of the average transport numbers in more concentrated solutions. This was done by measuring a series of diffusion potentials. From the equation—

$$\text{Diffusion potential, } E_d = 0{\cdot}058\,(1 - 2n_A) \log \frac{a_1C_1}{a_2C_2}$$

the mean value of $1 - 2n_A$ could thus be determined.

The measurement was carried out in a similar manner to that of the membrane potential, the place of the membrane being taken by a syphon tube containing the more dilute of the C_6H_5COONa solutions. No special care was taken to preserve a sharp boundary between dilute and concentrated solution, since, in the first place, no change of E was observed within a moderate time; such a change would have taken place if the progress of the mixing with time had been capable of producing it. Cumming (*loc. cit.*) also has been unable to detect any potential difference due to the opposition of a completely mixed and a sharp contact between two electrolytes.

The results indicate that the relation between E_d and $\log \frac{a_1C_1}{a_2C_2}$ is nearly linear, and that therefore there is a mean transport number which does not vary much with the dilution.

The e.m.f. between a 0·1 and 0·01 solution is, *e.g.*, almost identical with that between 1·0 and 0·1 solution:—

E(mv).	C_1.	C_2.	$\log a_1C_1 - \log a_2C_2$.
12·8	0·1	0·01	0·945
17·5	0·2	0·01	1·20
21·2	0·5	0·01	1·53
25·1	1·0	0·01	1·74
12·85	1·0	0·01	0·79
22·6	1·0	0·02	1·45

These results are shown by the lower line on the graph. The best linear equation connecting E and $\log \frac{a_1C_1}{a_2C_2}$ was calculated by the method of least squares, and it was found that—

$$E(\text{mv.}) = 1 + 13{\cdot}5 \log \frac{a_2C_1}{a_2C_2}.$$

On the above assumptions the linear graph should pass through the origin, actually it is +1 millivolt away. The average value of $1 - 2n_A$ is—

$$\frac{13{\cdot}5}{58} = 0{\cdot}234$$

and—

$$n_A = 0{\cdot}383.$$

The transport number of the anion therefore agrees w

with that calculated from the ionic mobilities at infinite dilution, *i.e.*, 0·388.

Membrane Potentials.

The potentials observed when the diffusing layer is on a parchment membrane are considerably higher than the ordinary diffusion potentials, although they do not in any case reach the value $E(\text{mv.}) = 58 \log \frac{C_1}{C_2}$ corresponding to $n_A = 0$, or a membrane impermeable to the benzoic anion. On the above assumptions the effect of the membrane appears to be to decrease the mobility of the anion compared to that of the cation.

The relation of $\log \frac{a_1 C_1}{a_2 C_2}$ to E is here also approximately linear, and from it an average transport number in the membrane has been calculated.

The magnitude of the deviations may be seen on the accompanying graph. They may perhaps be due in part to the uncertainty in the calculation of ionic concentrations from conductivities. The theory has also been somewhat severely tested by the employment of such different ranges of concentration. Thus it has been assumed that a fall of ionic concentration between 0·5 and 0·05 will produce the same e.m.f. as the fall between 0·2 and 0·02.

In the following table the total concentrations of the two solutions are given in the first column, C_1, C_2. The second column contains the logarithms of the ratios of ionic concentration, the third the observed e.m.f. in millivolts:—

C_1, C_2.	$\log \frac{a_1 C_1}{a_2 C_2}$.	E (millivolts).
0·202—0·1007	0·26	10·80
0·505—0·209	0·30	12·20
0·202—0·064	0·44	14·95
0·202—0·025	0·81	23·05
0·505—0·064	0·76	24·20
0·202—0·0212	0·98	28·25
0·501—0·0252	1·125	32·60
0·505—0·0245	1·14	34·45
0·202—0·012	1·13	35·10
1·010—0·023	1·39	37·25

The numerical constants of the linear equation:—

$$E = a + b \log \frac{a_1 C_1}{a_2 C_2}$$

are found to be:—

$$E(\text{mv.}) = 4 \cdot 53 + 24 \cdot 8 \log \frac{a_1 C_1}{a_2 C_2}.$$

Hence—

$$58(1 - 2n_A) = 24 \cdot 8$$

and—

$$1 - 2n_A = 0 \cdot 428 \quad n_A = 0 \cdot 286.$$

*It is remarkable that this graph does not, as in the case of diffusion potentials, pass almost through the origin but intercepts an ordinate of 4·5 millivolts. Pending further investigation the author is unable to suggest an explanation of this. For zero difference of concentration the observed E falls to zero. It may be that the function assumes other forms between the smaller differences of concentration observed (about 2 to 1) and zero difference.

For such differences in concentration as lend themselves to measurement the transport number of the anion is apparently decreased in the ratio $\frac{0 \cdot 286}{0 \cdot 388} = 0 \cdot 74$, *i.e.*, the transport number of the anion in the membrane is less than three-fourths of that in the free solution.

Further work on similar lines will, it is hoped, decide the applicability of the above hypothesis to other cases, and also whether it is true in general that the mobility of the slower ion is apparently checked by such a diaphragm.

This work was done at the Muspratt Laboratory of the University of Liverpool in 1913.

THE SCIENTIFIC WEEK.

(From Our Own Paris Correspondent).

EXTRACTION OF GERMANIUM FROM THE WATERS OF VICHY.

In a recent study M. Jacques Bardet announced that germanium is to be found among the rare bodies contained in the water of Vichy. Since then he has undertaken the separation of this exceedingly rare body. The new researches, in which he gives the results obtained, have just been presented before the Academy by M. Moureu. In treating 100 kgrms. of the earthy residue which is precipitated during the evaporation of Vichy water employed in the manufacture of salts, 100 kgrms. of earthy salts correspond to 250 tons of mineral water. In proceeding by separations regularly followed with the spectrograph, so as not to lose this precious metal, the author has managed to obtain 6 centigrms. of pure oxide of germanium. This result corresponds to a proportion of 24 hundred-millionths of a milligrm. per litre of water. This shows the sureness of the physico-chemical method in analysis. This kind of analysis may be compared to the extraction of radium, wherein also we proceed by separations, in following the operations with the electroscope. In the spectro-chemical analysis separations are also made, but they are followed with the spectrograph. Thanks to this new means it is possible to obtain infinitely small quantities of matters which it would never have been possible to isolate with the old methods.

TRANSMISSION TO A DISTANCE OF COLOURED PHOTOGRAPHY.

Telephotography is an invention of a relatively recent date. As is known, it consists in the transmission to a distance of photographs, drawings, plans, or sketches. Two different systems have been devised by Prof. Korn, of Munich, and by M. Edouard Belin, of Paris. An Italian engineer has tried to improve upon these methods. He has had the idea of transmitting telegraphically to a distance coloured photographs. His method consists in realising this transmission in three distinct and successive phases. In the first phase, for example, the orange-red colour will be transmitted, in the second green, and in the third the violet-blue colour. In this way the film of the receiving station will receive three different impressions in three separate times. This method can be realised in two ways:—(1) Either the coloured photograph will be placed on the turning drum of Korn's apparatus, this apparatus being lighted successively by a coloured source of the three different colours; or else (2) the photograph having been taken by means of an apparatus capable of obtaining in one single pose the images corresponding to the three fundamental colours, by successively transmitting these images lighted by white light. This method is also applicable to Belin's system of photography. For that it suffices to prepare three bichromated gelatin negatives, corresponding to the three fundamental colours, and to transmit them one after the other to the receiving station.

Institute of Metals.—*Portsmouth Conference.*—Portsmouth has been selected as the place of meeting for the Autumn Conference of the Institute of Metals. The Conference, which will be presided over by Engineer Vice-Admiral Sir Henry J. Oram, K.C.B., F.R.S., the President of the Institute of Metals, will be held on Thursday, September 10, and Friday, September 11, in the Municipal College, a number of important papers being read each morning. In the afternoon of September 10 a visit will be paid to Portsmouth Dockyard, and there will be a Dinner in the evening. On September 11 the afternoon function will consist of a Luncheon at the Cowes Works of Messrs. J. Samuel White and Company, the works afterwards being visited.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, May 28, 1914.

Sir William Crookes, O.M., President, in the Chair.

Papers were read as follows:—

"*Anomalous Trichromatic Colour Vision.*" By Prof. W. Watson, D.Sc., F.R.S.

It is shown from the results of measurements made on some forty subjects that anomalous trichromates are sharply divided into two distinct classes, and two experimental methods of distinguishing these classes are described.

One class corresponds apparently to a reduction form of ordinary trichromatic colour vision, and is characterised by want of definiteness when making certain matches. The other class cannot be considered a reduction form of normal trichromatic vision, but corresponds to an abnormal type of trichromatic vision in that one of the sensation curves occupies a displaced position in the spectrum. Colour matches obtained by this class of anomalous trichromates differ from the normal, but the accuracy with which they can be made is as great as in the case of the normal.

A curious fact as to the first class is clearly brought out by the measurements recorded, namely, that in the matches described, although a considerable band of the spectrum supplies a satisfactory match to these persons, one limit of this band always corresponds to the position which gives a correct match for the normal, although the band lies sometimes on one side and sometimes on the other of this position.

"*Diformdiol-peroxide.*" By Dr. H. J. H. Fenton, F.R.S.

The conditions of co-existence, and the mode of interaction, of hydrogen dioxide and formaldehyde are of some interest in connection with certain theories which have been advanced in order to account for the photo-synthesis of carbohydrates in the living plant. [Compare, for example, Bach (*Comptes Rendus*, 1893, cxvi., 1145), and Usher and Priestley (*Proc. Roy. Soc.*, 1906, lxxvii., 369, and lxxviii., 318)].

During the course of some experiments in this direction, it has been found that, under appropriate conditions, these two substances combine to form a compound $2H \cdot CHO \cdot H_2O_2$ which crystallises in large transparent plates or prisms. This compound explodes when warmed to about 75°, and takes fire if brought into contact with reduced iron or platinum black. It decomposes slowly in bright sunlight and appears to undergo some interesting changes, but it is stable if kept in the dark. In aqueous, or acetic acid, solution it gives the normal molecular weight for the formula indicated, and its condition at 0°, in aqueous solution, remains unchanged for forty-eight hours or more. If the aqueous solution is treated with platinum black the hydrogen dioxide is catalytically destroyed, and the freezing-point depression remains practically unchanged, indicating the dimeric form of the aldehyde, or else a corresponding mixture of the trimeric and monomeric forms (compare Aubach, *Chem. Centr.*, 1905, ii., 1081).

The general behaviour of the substance indicates that it is to be regarded as an "atomic" compound, in the ordinary sense of the term, rather than as a compound containing hydrogen dioxide of crystallisation.

It is most probable that the compound is identical with that which Legler, in 1881, obtained among the products of the slow combustion of ether.

"*Studies of the Processes Operative in Solutions. XXIX. The Disturbance of the Equilibrium in Solutions by 'Strong' and by 'Weak' Interfering Agents.*" By Prof. H. E. Armstrong, F.R.S., and E. E. Walker.

The effect of a large number of substances on the optical rotatory power of an aqueous solution of fructose has been measured and the views put forward in No. XXVI. of these studies with regard to the action of interfering agents have been confirmed and elaborated. "Strong" solutes, such as the sugars and metallic salts, increase the negative rotatory power of fructose, whereas "weak" solutes, such as the alcohols, ketones, and ethers, decrease it. The observed effect of the added substance ("the interfering agent") is regarded as the algebraic sum of two opposing factors:—

1. A diluent effect causing *dissociation* of hydrates and other complexes in solution.

2. An influence, opposite in effect to the first, depending on the reciprocal chemical attractive powers of the molecules of solvent and interfering agents promoting *association*.

A simple mathematical expression involving these two factors has been developed, by means of which (2) has been evaluated. This value is denoted by A. Thus calculated, A is found to be *very nearly proportional to the number of atoms of oxygen in the molecule*. The value of A, however, is increased by the presence of an ethylene linkage or of a phenyl group. In nitrogen compounds, A varies considerably with the mode of combination of the nitrogen. The same method of treatment has been adopted in analysing the influence of interfering agents on (1) the solubility of potassium chloride; (2) the rate at which cane sugar is hydrolysed by acids. The value of A is also correlated approximately with the influence which the solvent exerts on the rate at which chemical action takes place in solution.

"*Morphological Studies of Benzene Derivatives. VII. The Correlation of the Forms of Crystals with their Molecular Structure and Orientation in a Magnetic Field in the case of Hydrated Sulphonates of Dyad Metals.*" By Prof. H. E. Armstrong, F.R.S., and E. H. Rodd.

"*A Type-reading Optophone.*" By E. E. Fournier d'Albe, D.Sc.

A description is given of a new construction of the "optophone," an instrument capable of translating light action into sound, and so making light recognisable by means of the ear. The new instrument is intended to enable totally blind persons to recognise and "read" ordinary letterpress by means of the ear.

It consists essentially of a rapidly rotating disc perforated like a siren disc with several concentric circles of holes. A Nernst lamp is placed behind the disc with its filament stretched radially across the circles. The light, shining through the holes, gives regularly recurring flashes which, when of suitable frequency, can be detected by means of selenium and a telephone.

An image of this line of intermittently luminous dots is thrown upon the type to be read, and the light diffusely reflected from the type is received on a selenium bridge. As each dot has a characteristic note, the sound heard in the telephone will vary with every variation in the reflecting power of the surface under examination. As the letterpress is moved on in the direction of the line of type, the sound changes rapidly with every change in the shape of the letters, and with some practice the latter can be "read" by ear.

Type 5 mm. high can be thus read by means of an ordinary high-resistance telephone receiver. The effect becomes rapidly fainter as the type diminishes in size, but ordinary newspaper type is readable with the help of a highly sensitive Brown telephone relay.

"*An Application of Electrolytically-produced Luminosity, Forming a Step towards a Form of Telectroscopy.*" By L. H. Walter, M.A.

The author has investigated the conditions under which it should be possible to make practical use of the luminosity of anodes of alloyed aluminium forming part of a "valve" cell arrangement. The alloy known as "duralumin" is

found to give the best results, and with sodium tungstate solution as electrolyte, corrosion is practically eliminated when this alloy is used as the anode.

The difficulties with immersed anodes led the author to employ anodes which are completely dry, except as regards the front surface, which is kept wetted by means of a layer of electrolyte caused to flow down it in a continuous stream, the flow being distributed by using a transparent crêpe screen which clings to the anode surface. In this way, the anode being dry at the back, electrical connection can be directly established there, without the great care as to insulation otherwise needed.

This arrangement permits of the construction of an apparatus having a multiple anode, comprising a vast number of equal units in quite a small compass, each such unit being capable of being rendered luminous in any order or sequence desired and at a speed of some hundreds of times per second.

In the author's experimental apparatus there are over 5000 such separate units in a space the size of a cabinet photograph, or at the rate of over 24,000 per square foot —a number which it would hardly be possible to obtain by other means.

Such an apparatus is capable of being employed as a receiver in photo-telegraphy for the reproduction of pictures, &c., especially where these are received as electrical impulses. It constitutes a step towards one form of telectroscopy, the luminous reproduction at some receiver, of an object visible at some distant electrically-operated transmitter.

"*Axial Chromatic Aberration of the Human Eye.*" By P. G. Nutting.

"*Convection of Heat from Small Cylinders in a Stream of Fluid, and the Determination of the Convection Constants of Small Platinum Wires, with Applications to Hot-wire Anemometry.*" By L. V. King.

CHEMICAL SOCIETY.

Extra Meeting, May 25, 1914.

Prof. W. H. Perkin, Sc.D., LL.D., F.R.S., President, in the Chair.

This meeting was held in the Theatre of the Royal Institution, by kind permission of the Managers.

The President, in opening the proceedings, said: We are assembled in this historic place to pay a tribute of respect to the honoured and revered name of Faraday, and, at the same time, to add another to the list of illustrious men who have served as Faraday lecturers in the past. I do not need to introduce Prof. Arrhenius to such a gathering as this. Many of you know him personally, and all of you are aware of the great influence which his brilliant and far-reaching generalisations have had on the development of modern science. I have therefore great pleasure in calling upon Professor Arrhenius to deliver the Faraday Lecture.

Prof. Arrhenius then delivered the Faraday Lecture, of which the following account is an abstract. (Full Report, *Trans.*, 1914, p. 1414).

Most of my predecessors in this position, being mindful of the far-reaching importance of Faraday's discoveries, have treated general questions connected with Faraday's work, and bearing on our fundamental conceptions of matter. It is most opportune for me that the chief investigation made by myself falls within the great domain of electrochemistry, which Faraday enriched in a marvellous manner, especially by the discovery of his law, which is fundamental to all later work in this chapter of Science. The work on which I have to speak to you also concerns the constitution of matter. Solutions, especially those of salts, are of a peculiar character. Gay-Lussac, the most prominent physicochemist of his time, paid special attention to solutions, and reached some conclusions which apparently are very modern. In his remarkable memoir of 1839, "Considérations sur les forces chimiques," he says: "As the effects of affinity do not change with temperature, whereas dissolution (solubility) is in a high degree dependent upon it, it is very difficult to avoid the assumption, that in dissolution as well as in evaporation, the product is essentially limited, at a given temperature, by the number of molecules which are able to exist in a certain volume of the solvent. They are separated from this, just as gaseous molecules are precipitated, by a lowering of temperature. . . . Dissolution is therefore in a high degree connected with evaporation, namely, in this respect, that both of them depend on the temperature and are subject to its variations. Hence they ought to show, if not a complete identity in their effects, at least a great analogy."

Here Gay-Lussac is a precursor of van 't Hoff, who, forty-five years later, developed in such a masterly manner the idea of the analogy between matter in the dissolved and in the gaseous state.

In 1883 I investigated the electrical conductivity of different electrolytes, and came to the conclusion that the molecular conductivity increases with dilution, because the number of conducting molecules increases at the expense of the other, non-conducting, molecules. At infinite dilution all molecules of an electrolyte are conductors. This hypothesis led to the following chief conclusions. The molecular conductivity at infinite dilution is an additive property for all electrolytes, and not only within certain groups of electrolytes of similar composition, as maintained by Kohlrausch for the molecular conductivity of diluted electrolytes. According to the thermo-chemical data given by Berthelot and Thomsen, the stronger an acid is the greater is its molecular conductivity. The electrically conducting molecules are therefore the same as the chemically reacting molecules, the nature of which is characterised by Williamson and Clausius. At infinite dilution all acids must therefore be of the same strength. In accordance with these ideas, the velocity of reaction caused by an acid is proportional to its number of electrically conducting molecules per unit volume. This assertion could only be verified qualitatively in some very few cases, because experimental determinations were wanting. The heat evolved on neutralising one equivalent of an acid consisting of only conducting molecules with a base of similar kind is always the same and equal to the heat produced when one equivalent of conducting molecules of water is transformed into one equivalent of non-conducting molecules. Therefore the heat of neutralisation of strong acids with strong bases at high dilution, as in the experiments of Thomsen, when they are composed almost entirely of conducting molecules, is very nearly the same for all acids and bases in equivalent quantities. When a salt such as potassium ferrocyanide, $K_4C_6N_6Fe$, the ions of which are $4K$ and C_6N_6Fe, enters into a chemical reaction with another salt in aqueous solution, there are formed only ferrocyanides and potassium salts, but not ferrous or ferric salts, because the result is always a rearrangement of the ions.

Such were the conclusions drawn from a rather small number of experimental data, and I do not wonder that my colleagues refused to take notice of these ideas, which seemed absolutely incompatible with the prevailing conceptions regarding the chemical nature of salts. Very soon after my memoir had appeared, Ostwald published measurements of the conductivity of thirty-four acids, and showed that the molecular conductivity of the acids is very nearly proportional to the velocity of reaction in catalytic processes (inversion of sucrose, hydrolysis of esters) caused by these acids. A little later he also proved that the relative strength of weak acids, as compared with that of strong acids, increases with dilution, so that all acids show a tendency to become of equal strength in infinite dilution. Both of these laws were predicted in my memoir of 1884. Then there were two different phe-

nomena, the molecular conductivity and the chemical activity of acids, which quantitatively led to the same conclusion.

This was not, however, sufficient evidence to support the bold hypothesis that salts, including acids and bases, are to a great extent dissociated into their ions. Fortunately, I had not long to wait for further evidence. In 1886 van 't Hoff published his revolutionising memoir on the analogy of dilute solutions to gases. There he showed that Raoult's measurements on the freezing point of aqueous solutions pointed to the fact that the influence of one molecule of a salt, such as potassium chloride, in great dilution, was double that of a simple molecule (alcohol, ammonia). This fact was wholly analogous to the fact that some substances, for example, ammonium chloride and phosphorus pentachloride, in gaseous state per molecule exert a pressure which is double as great as that produced by common undissociated gases. According to the law of Avogadro, the latter circumstance could only be explained by the hypothesis that the molecules of such substances as ammonium chloride or phosphorus pentachloride are dissociated, when vaporised, into two molecules, namely, ammonia and hydrogen chloride or phosphorus trichloride and chlorine, respectively. The experimental proof of this hypothesis was also given by v. Pebal and v. Than in 1862 and 1864. From analogy to this experience, there seemed no other possibility open to explain the abnormal freezing point of solutions of potassium chloride than to suppose that the molecules of this salt were for the greater part dissociated into their ions K and Cl. Thus Raoult's measurements of the freezing point gave a means of determining the degree of dissociation of a great number of substances, the aqueous solutions of which he had investigated. By the aid of the measurements of Kohlrausch, regarding the molecular conductivity of different substances, it was possible to make another independent determination of their degree of dissociation. The two methods gave values which agreed very well with each other when dilute solutions (generally 1 per cent) were examined. A thorough examination by A. A. Noyes and Falk (*Journ. Am. Chem. Soc.*, 1912, xxxiv., 455) leads to the conclusion that for electrolytes consisting of two univalent ions the difference does not reach more than 2 per cent if the solutions are 0·1 normal or less. The same is also valid for potassium sulphate and lead nitrate. For salts such as calcium chloride, calcium nitrate, magnesium chloride, &c., the deviation is much greater, the freezing-point method giving too high values. The deviation seems to have something to do with the hygroscopic nature of most of these salts. For copper sulphate and similar salts I have found that the said method gives too low values, which is due to the formation of double molecules, as Hittorf observed as early as 1859. The change of the molecular composition with dilution is seen from the simultaneous change of the rate of migration. The chief point, however, is that salts (strong acids or bases included) consisting of two univalent ions give the molecular depression $2\times1{\cdot}85=3{\cdot}7$, salts of one bivalent ion with two univalent ions give $3\times1{\cdot}85=5{\cdot}55$, salts of one tervalent ion with three univalent ions give $4\times1{\cdot}85=7{\cdot}4$, &c., whereas non-electrolytes give 1·85, all in extreme dilution. In extreme dilution the dissociation is complete.

Further, it was possible to calculate the degree of dissociation from the strength of the catalytic action of the acids, and in 1889 I showed that, within the limits of the errors of observation, the values found in this manner agree wholly with the values deduced from the magnitude of the electrical conductivity.

Of the three methods of determining the degree of electrolytic dissociation, that founded on the measurement of the electrical conductivity has always been preferred to the other two. This choice is chiefly based on practical reasons, because the method is applicable to solutions in all solvents, and because it is possible to determine the conductivity with an accuracy of about 0·2 per cent up to the highest dilutions investigated—about 0·0001 normal. The high dilutions are just those by which the trustworthiness of the theory ought to be controlled.

There was also a fourth fundamental fact in favour of the dissociation theory, namely, the additive properties of solutions of electrolytes. Certainly there are other additive properties valid also for non-dissociated substances; for example, the mass of a substance is an absolute additive property, because it is equal to the sum of the masses of the constituents. If we except the mass, however, the additive character is far less prominent for undissociated molecules than for electrolytes.

The additive properties of solutions of electrolytes have for a long time attracted the attention of physico-chemists, because they are so strongly pronounced. If the electrolytes are dissociated into their ions, it is quite clear that the properties of their solutions may be regarded as the sum of the properties of the solvent and of the ions. The additive property which is most familiar to the chemist is the chemical reaction of solutions of electrolytes. All salts containing chlorine as ion give the reaction "of chlorine," as it is said, but it would be more exact to say "of the chlorine ion." But chlorates, containing the ion ClO_3, perchlorates with the ion ClO_4, the numerous chloro-salts of cobalt, platinum, iridium, &c., in which the chlorine is placed in the inner sphere, according to Werner, and all the salts of the chloro-substituted organic salts, do not give "the reaction of chlorine."

On these four strong foundations: the freezing-point, the electrical conductivity, the chemical reactions and other additive properties of electrolytic solutions, as well as the strength of acids and bases, it was possible to erect a thoroughly solid building capable of sustaining attacks from without, and this building is the theory of electrolytic dissociation, first enunciated in 1887.

As a general conclusion, it may be stated that the difficulties inherent to the theory of electrolytic dissociation have been overcome only within a very recent period, when the observed facts have been more closely examined. It is now our task to investigate the causes which interfere with the simple laws in more concentrated solutions, and to find those other theoretical laws which govern these deviations.

In presenting the Faraday Medal to Prof. Arrhenius at the conclusion of the lecture, the PRESIDENT said: Prof. Arrhenius, it is now my very pleasant duty to hand you the Faraday Medal, the highest honour the Society has to confer, and I should like to add an expression of our deep regard for you as an honoured member and our respect for you as a man of science.

Sir WILLIAM CROOKES, in proposing a vote of thanks to the lecturer, said: Mr. President, Ladies and Gentlemen,—With deep satisfaction I rise to propose a vote of thanks to our distinguished guest, and to offer our congratulations to him on his very interesting lecture. Prof. Arrhenius has made his subject glow. He has drawn freely upon his vast stores of knowledge, and he invites us to share in the astonishing results of his researches. We are glad to welcome him in this country, where, indeed, he is already well known, and glad to felicitate him upon his command of our language, and on the fluency which is so marked a feature of his speech. We find it peculiarly fitting that the Faraday Lecture should be delivered by the Director of the Nobel Research Institute.

There is perhaps no need for me to remind you of Prof. Arrhenius' scientific work. It is known to many how, more than a quarter of a century ago, he contributed to science one of its greatest generalisations, which he has now placed before you here, and which, after much strife, has taken its place as one of the corner-stones of chemistry. In early days I well remember the hostile objections. The hot controversies that raged reminded one of one of Ruskin's whimsical sayings—that most matters of

any consequence are not merely to be regarded from two points of view, but are really three- or four-sided, or even polygonal, and "trotting round a polygon is stiff work for people who are in any way stiff in their opinions."

We can hardly listen to a Faraday Lecture without letting our thoughts dwell upon the great Faraday himself, and comparing him and his work with that of his eulogist, our illustrous guest. Faraday's work, like that of Arrhenius, lay chiefly in the borderland of chemistry. He was the pioneer in the region of physical chemistry, which of late years has revealed such boundless stores of wealth. There is an obvious close connexion between his electrochemical laws and Arrhenius' theory of electrolytic dissociation. Faraday was a true epoch-maker, and a most striking example of the supreme value of those who cultivate science for its own sake without ulterior motives and without thought of the commercial value of their discoveries. How enormous is the value of Faraday's work the world has not yet by any means realised, but if in later times an adequate appreciation of its far-reaching results comes to be written, I am almost tempted to suggest that its title might be "Civilisation in the Making."

Arrhenius has suggested to us how worlds may be made, and surely Faraday did more than any one single individual to show us how to civilise worlds when made. A further resemblance may be observed between our guest and Faraday, and that is the remarkable gift of clear exposition. Not many of those present, I suppose, ever heard Faraday lecture; but some of you know of his fame in exposition, and I can assure you from personal experience that it has not in the slightest degree been exaggerated.

Prof. Arrhenius' later work in immuno-chemistry, and his researches into the action of toxins and anti-toxins, have challenged the attention of the scientific world, and still more recently his investigations in cosmogony have startled staid scientific men. "Worlds in the Making" is a title bound to catch the mind's eye, and those of you who have read the book, and the later volumes on the Life of the universe, will no doubt agree with me as to the absorbing interest of the subject, the cogency of the arguments, and the skill with which they are handled. The world is deeply in need of researchers both of the type of those whose genius is characterised by that fertility of resource in experimental investigation exhibited by Faraday, and of the type of Arrhenius, whose gifts of intrepid speculation and imagination enable him to reveal new worlds of thought. Both are revolutionaries and founders of new kingdoms. Both types are rare. Both are "world compellers," and the world's debt to them is incalculable. I think we may begin to look hopefully forward to a time of fuller recognition of scientific genius and deeper appreciation of the value of scientific work, and certainly the British nation will not be found in the rear-guard in that desired advance. Once again let us offer our hearty thanks to Prof. Arrhenius, and assure him of our genuine appreciation of his masterly exposition of, I might almost say, a sensational chemical problem.

Sir William Tilden, in seconding the vote of thanks, said: Ladies and Gentlemen,—I am one of those who cling tenaciously to the principle of submission to properly constituted authority. Consequently, when the President preferred a request that I should stand in this honourable position of seconding the vote of thanks to the Faraday Lecturer, which has been so eloquently proposed by the President of the Royal Society, I looked upon it as a command, and concealed my own misgivings, feeling as I did that I could not be regarded as a representative of any body of chemical opinion on the present occasion. We are here to-day to celebrate the great name of Faraday. A celebration of the same kind has been held by the Chemical Society on, I think, ten previous occasions, and it would be impossible, as you realise, no doubt, for the Society effectively to carry out its wish except with the aid of our eminent colleagues and friends who have visited us from abroad on all these previous occasions.

We have had assistance from France, from Germany, from Italy, and from the United States. On the present occasion we have the great pleasure of welcoming among us, not for the first time—for his face and figure are familiar to everybody in London—we have the great pleasure of receiving here to-night and welcoming a representative of that great country which, I am almost tempted to say, has done more—but at any rate has contributed not less—than any other country to the advancement especially of chemical science.

It is only necessary to remember that Scandinavia has produced Scheele and Berzelius, besides many others whose names will doubtless occur to you. I think you will agree with me that our friend who has just delivered the Faraday Lecture is a worthy successor to his great countrymen whose names I have just mentioned.

I think the first qualification in a Faraday Lecturer must be that he has by his own work and his own researches contributed to the advancement of that department of science with which Faraday's name is, and has always been, associated; and in this case that quality is presented eminently by the Faraday Lecturer.

With regard to the theory of electrolytic dissociation, which has been the subject of the discourse this evening, my experience, perhaps, is very much that of a good many others, and probably the majority, in this room. When it first began to be discussed seriously, close upon twenty years ago, I confess I was among those who were strongly hostile. But I felt, as time went on, that I had to lay before my students—for I was a teacher in those days—at any rate an exposition of what other people believed in regard to this department of the theory of chemistry; and it was my experience that by merely presenting those views, so new and so unacceptable as they were to me at that time, I gradually got to feel that they were inevitable, and that they were absolutely necessary. One was forced to consider all the pros and cons, and ultimately I was led to a conviction of the very valuable character of the theory that I was then expounding. Of course, the theory of electrolytic dissociation, like every other theory which has become established in the fabric of theoretical chemistry, must pass through, has passed through, and will continue to pass through the same kind of experience as other theories. It has met, first of all, strong opposition and violent criticism, but it has ultimately been accepted, and all that remains is to clear away the few comparatively small difficulties.

At the same time, I always feel, and I hope most teachers feel, that every theory which we accept is bound to be modified more or less as time goes on. If not actually abolished, it will at any rate be modified very considerably in favour of something which is more comprehensive, and perhaps illuminated by a large number of new facts at present unknown to us.

I need scarcely say that I thank the President for allowing me the distinguished honour of standing here on this occasion, and I support most cordially the proposition which has been laid before the meeting by the President of the Royal Society.

The Chairman having put the vote to the meeting, it was carried with acclamation.

Prof. Arrhenius, in acknowledging the vote of thanks, said: Amongst learned societies, the Chemical Society was one of the very first which lent me support and gave me encouragement. It has therefore been a great pleasure and favour to me to come back to London on repeated occasions and speak to and see my many dear friends in this Society. Every time I returned I felt that your kindness and friendliness towards me had increased. To-day it has reached its maximum, when you have conferred upon me the greatest honour you can give. I cannot express my deep feelings of gratitude towards the Society as I would wish, and I must confine myself to saying that you have my warmest and deepest thanks.

SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

Ordinary Meeting, June 3, 1914.

Mr. Leonard Archbutt in the Chair.

Certificates were read for the first time in favour of Messrs. John Kent Crow, 43, Westcombe Park Road, Blackheath, S.E.; and Horace Finnemore, Pharmaceutical Laboratory, Guy's Hospital, S.E.

Certificates were read for the second time in favour of Messrs. William Roscoe Hardwick; Harold Fletcher Hills; and Robert Hindle Kay.

The following papers were read:—

"*Insoluble Bromide Value of Oils and its Determination.*" By Alexander Gemmell.

The author gives an account of work carried out to obtain concordant results of this value. His conclusions are that the glycerides should not be directly brominated, but that an ethereal solution of the fatty acids should be used. The bromine content of the precipitates obtained has also been investigated, and he shows these to consist essentially of mixtures of bromo derivatives, not of pure hexa-bromides. The value determined for various oils is also given.

"*Determination of Iridium in Platinum-iridium Alloys.*" By G. O. Bannister and E. A. du Vergier.

Gives details of a method of differentiating between platinum, platinum-iridium, and platinum-rhodium alloys by noting the appearance of beads obtained by cupelling small quantities of the materials with silver. The presence of rhodium is indicated by a large amount of spitting of the bead, and the presence of iridium by the fact that the bead assumes a more spherical shape, whilst the surface is seen under a low power microscope to be covered with markings indicative of internal stresses.

The results of the determination of the solubility of platinum-iridium alloys in aqua regia are given for a series of alloys containing from 2·5 to 25 per cent iridium.

Two methods for the accurate determination of iridium in platinum-iridium alloys are described and results obtained by these methods are compared.

The first method consists in cupelling with silver, parting with sulphuric acid to obtain separate particles of iridium and platinum, and then dissolving the platinum in dilute aqua regia and weighing the iridium. The second method consists in melting the alloy with pure lead, dissolving the lead in nitric acid, and separating the platinum and iridium as before with dilute aqua regia.

"*Symbolical Representation of Analytical Operations.*" By L. Gowing Scopes.

A scheme is proposed for representing analytical processes by means of symbols somewhat similar in application to chemical equations. A list of useful symbols is given, and several typical operations are worked out. Its probable uses and extensions are indicated.

"*The Properties of some Chlorhydrocarbons and their Uses in Chemical Analysis.*" Part II. By L. Gowing-Scopes.

The author discusses the reaction between chlorethanes and phenylhydrazine. He finds the conditions vary too much to use the reaction for estimating these bodies, with the exception of hexachlorethane.

A method is given for the estimation of the chlorethanes by the action of $n/3$ alcoholic potash in the cold and the subsequent titration of the halide formed. Under these conditions hexaclorethane does not react and the chlorethylenes do not interfere.

A colorimetric method for estimating hexachlorethane is under investigation.

"*Changes in the Character of Fats during the Process of Cooking.*" By Helen Masters and Henry L. Smith.

When fats are cooked with flour, as in pastry, hydrolysis of the fat is but slight, changes of the same type as in the blowing of oils, however, occur. The iodine value decreases, the acetyl value and the refractive index increase. Apparently the fat becomes more hydroxylated, but no definite ratio between the decrease in the iodine value and the increase in the acetyl value can be observed. Oxidation of the fat also takes place, the fat becomes darker and more viscous and "oxidised" acids are formed. All these changes are more marked the longer the pastry is cooked. These changes have been observed with cotton-seed oil and butter-fat, butter-fat changing less than the more unsaturated oil. In the case of cotton seed oil there is also a marked increase in the volatile acids. Except in the case of very thin pastry or when it has been over-cooked the changes are small, and would not interfere with the detection of adulteration or substitution.

"*Chief Cause of the Loss on Sulphuric Anhydride and of Chlorine by Ashing Substances containing these Constituents.*" By James O'Sullivan.

The author finds (1) that when either sulphate of calcium, potassium, or sodium are present with organic matter, an ash is obtained containing only slightly less sulphuric anhydride than was present, but if magnesium sulphate is present then the ash contains only a small proportion of the sulphuric anhydride; (2) that in the presence of magnesium sulphate and organic matter the chlorides may be completely destroyed; (3) the presence of phosphates has no influence on the amount of sulphuric anhydride found in the ash; (4) that if the ash of a substance is alkaline and contains magnesium oxide and no carbonate, then neither the chlorine nor the sulphuric anhydride found in it can be safely taken as anything like a measure of either of these present in the substance.

"*Note on the Presence of Sulphates in Flour.*" By R. A. Cripps and A. G. Wright.

The purport of this note was to show that sulphates exist as such in flour; direct determination in samples yielded 0·0069, 0·0076, 0·0084, 0·0084, 0·0069, and 0·0103 per cent, the last being a "whole-meal" flour.

The reason for the low results obtained by determination *in the ash* was stated to be the action of the acid phosphates of the flour upon the sulphate (or sulphide) at the low red heat required for ignition, experiments with the potassium acid phosphates mixed with sulphate of potassium or calcium indicating the complete volatilisation of the SO_3.

The proof of presence of sulphates naturally in flour might be of considerable importance in legal cases of addition of "improvers."

NOTICES OF BOOKS.

Modern Steel Analysis. By J. A. Pickard, B.Sc. (Hons. Lond.), A.R.C.Sc., A.I.C. London: J. and A. Churchill. 1914.

This little book will be useful to those who want concise directions for determining the most important constituents in steels; it is written for the practical man, and contains no superfluous details or lengthy discussions of trifling modifications of procedure. A short introductory section deals with general methods and gives some hints for economising time and saving labour in analysis; various pieces of apparatus which the author has found useful are described, and methods of sampling are briefly treated. In the special part the author has employed the space at his disposal judiciously, giving alternative methods for constituents of greater importance; in all cases rapidity of performance is taken into consideration in recommending certain estimations. The methods recently worked out by the author for cobalt, which is now being used for high speed steels, are described, and the many hints embodying the results of the author's personal experience of the processes described will be useful to the inexperienced analyst or student.

Clean Water and How to Get It. By ALLEN HAZEN. Second Edition. New York: John Wiley and Sons, Inc. London: Chapman and Hall, Ltd. 1914.

THIS book gives a readable account of the means adopted in many American cities to obtain a pure water supply. Some account is also given of methods of purification, the storage of filtered water, and the use and measurement of water. The information relates chiefly to American processes, but some questions of general interest are discussed, and the results of American experience are compared with that of European engineers and sanitary authorities. In the new edition chapters have been added on red water troubles and how to prevent them and upon the disinfection of water supplies.

Trade and Technical Education in France and Germany. London: P. S. King and Son. 1914.

THIS report by Mr. J. C. Smail, Organiser of Trade Schools for Boys, describes the author's personal observations and investigations of the state of professional trade education in Paris, Munich, Leipzig, and Berlin. Mr. Smail spent some time in each of these cities, studying the different systems of technical education, and was given every facility to make himself thoroughly acquainted with the scope and working of the trade schools. His conclusions are particularly interesting, and deserve careful consideration on the part of educational authorities. Syllabuses of the courses of instruction are given in the report and details of the training of special teachers. The excellent results of the system of compulsory continuation classes in Germany are pointed out, and it is shown that the cost per student hour of the same kind of instruction does not materially differ in Paris, Munich, Berlin, and London.

Röntgen Patterns of Boracite obtained above and below its Inversion Temperature. By Prof. H. HAGA and Prof. F. M. JAEGER. Amsterdam: The Royal Academy of Sciences. 1914.

THIS paper gives a short account of the apparatus used by the authors in studying the transmission of Röntgen rays through plates of boracite crystal at different temperatures, and describes the results of experiments in which the time of transmission was from two to three hours, and the temperature was raised to about 300°. Plates are given illustrating the patterns obtained at 18° and at 303°, and the significance of the results is very briefly discussed.

Blowpipe Analysis. By NICHOLAS KNIGHT. Fifth Edition. Mount Vernon, Iowa: Cornell College. 1914.

THESE notes on blowpipe analysis contain explicit directions for the detection of bases by flame tests and by ignition on charcoal before the blowpipe. The author gives beginners many hints which will prevent them from falling into common errors, and equations are added when the reactions are at all complex. Wet tests for acids are also given, including some common organic acids. The notes will be very useful for elementary students, for whom they will provide a good foundation for more detailed and difficult work in qualitative analysis.

Stereochemie. ("Stereochemistry"). By Dr. E. WEDEKIND. Second Edition. Berlin and Leipzig: G. J. Göschen. 1914.

THE science of stereochemistry has made very rapid advances since 1904, when the first edition of this little work was issued, and it has been found necessary to revise many of the details and add very considerably to the information given in it. In its present form it is a convenient little handbook in which the fundamental principles of the subject are clearly explained. All the most recent advances are discussed, as for example the stereochemistry of pentavalent nitrogen and the work of Werner on the optical activity of inorganic compounds, and the book undoubtedly supplies a need for a thoroughly scientific and concise treatment of stereochemistry.

Rothamsted Experimental Station. Annual Report for 1913. By E. J. RUSSELL, D.Sc., Director. Harpenden: D. J. Jeffery. 1914.

THIS annual report contains accounts of the work done on the farm and in the laboratory and pot culture house at Rothamsted during the year 1913. The research work which has been brought to a satisfactory conclusion and published includes a method of estimating carbohydrates, especially in plant extracts, by Messrs. Davis and Daish, and investigations of the soil solution and the mineral constituents of the soil, while further work has been done on the sterilisation of the soil and the growth of plants in partially sterilised soils. The Director of the Station, Dr. E. J. Russell, wishes to draw attention to the fact that the Lawes and Gilbert Centenary Fund is not yet closed, there still being £950 to raise before the new laboratories can be built, and the Committee is particularly anxious to clear off this last sum and begin building operations at an early date. The value and importance of the work which has been and is being done at Rothamsted can hardly be overestimated, and the data which have been accumulated there have no counterpart anywhere else in the world.

Principes d'Analyse et de Synthèse en Chimie Organique. ("Principles of Analysis and Synthesis in Organic Chemistry"). By M. HANRIOT, P. CARRÉ, A. SEYEWETZ, E. CHARABOT, and A. HÉBERT. Paris and Liège: Ch. Béranger. 1914.

THIS book is volume v. of the Encyclopædia of Applied Chemistry which is in course of publication under the editorship of Professor C. Chabrié, of the Sorbonne, and for the preparation of which some of the most distinguished of French chemists have collaborated. The aim of the authors has been to discuss and explain general ideas and principles rather than to enter upon minute descriptions of the details of processes, and each section has been written by an expert who has specialised in the branch which he discusses. The general principles of analysis are treated by M. Hanriot and the properties and preparation of pharmaceutical products by M. P. Carré. The chapters on the synthesis of dyes have been written by M. A. Seyewetz, and give a fairly detailed account of general and special methods of preparation. The extraction of perfumes and the production of artificial perfumes are also treated and a short section is devoted to the study of saponification.

La Silice et les Silicates. ("Silica and the Silicates"). By HENRY LE CHATELIER. Paris: Hermann et Fils. 1914.

THIS treatise on silica and the silicates gives a detailed account of the chemistry of these important compounds. The chemical properties of silica and its hydrates are first described, and the following chapters deal with the physical properties of quartz, polarisation, double refraction, &c., being discussed at great length, while other forms of silica are treated rather more shortly. The general properties of different glasses are subsequently described, and chapters are devoted to the metallic silicates, which are admirably treated from a descriptive point of view. A discussion of the scientific aspects of the ceramic industry occupies another chapter. Details of manufacturing processes are not included, but a general outline of the principles upon which they are based is provided.

Rapport sur l'Unification des Abréviations Bibliographiques dans les Mémoires de Chemie. ("Report on the Unification of Bibliographic Abbreviations in Chemical Memoirs"). By Prof. PH. A. GUYE. Geneva: Albert Kündig. 1914.

THERE is probably no need to call attention to the many advantages which would follow the adoption of a uniform system of abbreviation of the titles of journals, and the report of the proceedings of the third session of the "Association Internationale des Sociétés Chimiques," held

in Brussels at the Solvay Institute in September, 1913, will undoubtedly win the hearty approval of chemists. After some short discussion of the anomalies and difficulties involved. Prof. Guye details the proposal of the Council to invite the co-operation of editors and authors in the adoption of a uniform system of abbreviation of titles, and explains briefly how it is proposed that the Council should join with the Council of the International Catalogue of Scientific Literature to draw up a suitable and convenient list of abbreviations which, when accepted, will henceforward be regarded as international.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Bulletin de la Société Chimique de France.
Vol. xv.-xvi., No. 8, 1914.

Specific Rotatory Power of Camphor Dissolved in Olive Oil.—Henri Malosse.—The specific rotatory power of camphor in olive oil increases with the dilution. If q is the number of grms. of oil in 100 grms. of solution the increase is almost negligible when q lies between 75 and 83, slow if q lies between 83 and 90, more rapid if q lies between 90 and 25, very rapid if q is >95.

Composition of Gaseous Mixtures Resulting from the Action of Water on Carbides of Uranium and Thorium.—P. Lebeau and A. Damiens.—With the same sample the action of water upon the carbides of uranium and thorium gives comparable quantities of gaseous mixtures of very similar composition. With a graphitic and a non-graphitic carbide of uranium, however, the results are very different. In the latter case the reaction takes place much more slowly, and the hydrogenation of the hydrocarbons is more complete, as is shown by the increase in the proportion of hydrocarbons and the diminution of the quantity of hydrogen.

Action of Water upon Carbides of Rare Earths.—A. Damiens.—When water acts upon the carbides of cerium, lanthanum, neodymium, praseodymium, and samarium no methane is formed, the hydrocarbons obtained being acetylene, allylene, vapours of heavier hydrocarbons, ethylene, and ethane. The liquid hydrocarbons formed very readily fix oxygen in the cold. The systematic study of the oxides shows that they are the hydrates of sesquioxides, and the reaction takes place according to the equation $C_2M + 3H_2O = M(OH)_3 + C_2H_2 + H$. The hydrogenation of acetylene gives ethane and ethylene.

Products of Incomplete Reduction of Ceric Oxide.—A. Damiens.—The reduction of ceric oxide by carbon takes place in three stages:—

(i.) $CeO_2 + C = Ce_2O_3 + CO$.
(ii.) $Ce_2O_3 + 9C = 2CeC_3 + 3CO$.
(iii.) $CeC_3 = CeC_2 + C$.

The compound described by Sterba as an oxycarbide does not appear to possess the formula, CeC_22CeO_2, which he ascribed to it. The author obtained red products which are mixed crystals of the carbide CeC_3 and of fused cerous oxide.

Atti della Reale Accademia dei Lincei.
Vol. xxiii. [i.], No. 7, 1914.

Modification of Kjeldahl's Method.—L. Marino and F. Gonnelli.—The modification of Kjeldahl's method proposed by Oefele leads to inaccurate results for the percentage of nitrogen, the found and theoretical values differing by as much as 1 per cent. The authors find that more accurate results are obtained by boiling the organic substance (about 1 grm.) with 20 cc. of concentrated sulphuric acid in presence of about 7 grms. of potassium sulphate and 0·2 grm. of V_2O_5, until an emerald green solution is obtained.

MISCELLANEOUS.

Presentation.—Dr. F. B. Power, Director of the Wellcome Chemical Research Laboratories, was the recipient of an interesting presentation on June 5. This took the form of an illuminated address, the design of which was based upon a very beautiful folio in a Fourteenth Century manuscript copy of the Wyclif Bible. The presentation was made by Mr. G. E. Pearson on behalf of the leading members of the staffs of the scientific and commercial enterprises which owe their initiative to Mr. Henry S. Wellcome. The address, which tenders the congratulations and good wishes of the donors on the occasion of Dr. Power's receipt of the honour of the Hanbury Medal, was accompanied by an exquisitely bound blue morocco volume of autographs.

MEETINGS FOR THE WEEK.

Thursday, 25th.—Royal Society. "Note on Mr. Mallock's Observations on Intermittent Vision," by S. P. Thompson. "Variation of Electrical Potential across a Semipermeable Membrane," by F. G. Donnan and G. M. Green. "Potential of Ellipsoidal Bodies and the Figures of Equilibrium of Rotating Liquid Masses," by J. H. Jeans. "The 27-Day Period in Magnetic Phenomena," by C. Chree. "Electrification of Water by Splashing and Spraying," by J. J. Nolan. "Attempts to produce the Rare Gases by Electric Discharge," by T. R. Merton. "Analysis of Gases after Passage of Electric Discharges," by O. C. G. Egerton.

Erratum.—P. 288, col. 1. In "Action of Chloroform on Metallic Sulphates," line 8, *for* "$MnSO_4$, 450," *read* "$MgSO_4$, 450°."

THE CHEMICAL NEWS.

VOL. CIX., No. 2848.

THE PREPARATION OF EYE-PRESERVING GLASS FOR SPECTACLES.*

By Sir WILLIAM CROOKES, O.M., F.R.S.

(Concluded from p. 291).

Glass 240.

FURTHER experiments with biotite showed that its special property was due to the iron protoxide it contained, and another glass was therefore made in which the iron could be introduced in the form of a definite salt of known composition. Ferrous oxalate was chosen, the proportions being as follows:—

Raw soda flux	90
Ferrous oxalate, $FeC_2O_4 2H_2O$ ..	10
	100

The glass made from this material does not cut off quite so much of the heat rays as the one prepared from biotite, the rays obstructed being 88 as against 94 per cent. But the ultra-violet is entirely intercepted, the limit being λ 3950. It transmits 36 per cent of the luminous rays. It is of a smoky green colour. The tintometer numbers are:—Yellow, 4·0; blue, 4·0.

Glass 246.

This is a glass made on a larger scale at the Whitefriars Glass Works, and of the same composition to start with as Glass 240, namely, 10 per cent of ferrous oxalate with raw soda flux. At the suggestion of Mr. Harry Powell a small quantity of red tartar and powdered wood charcoal was added to prevent oxidation; the resulting glass is sage-green in colour, a plate 2 mm. in thickness cuts off ultra-violet rays down to λ 3800, its opacity to heat radiation is 98 per cent, and it transmits 27·6 of the incident light. The tintometer numbers are:—Yellow, 5·5; blue, 11·0.

A plate of this glass 1 mm. thick cuts off the ultra-violet rays down to λ 3550, its opacity to heat radiation is 83 per cent, and it transmits 47·9 per cent of the incident light. The tintometer numbers are:—Yellow, 2·25; blue, 5·0.

Glass 247.

Raw soda flux	92·00
Cerium borate	6·30
Nickel oxide	0·04
Ferric oxide	1·60
Chromic oxide	0·06
	100·00

Glass 247 has a faint green tint and is practically opaque to the ultra-violet rays, the limit being λ 3620. It obstructs 29 per cent of the heat radiation, and transmits 71 per cent of the luminous rays. The tintometer numbers are:—Yellow, 2·0; blue, 2·0.

Glass 248.

Fused soda flux	94·60
Cerium nitrate, crystallised	4·72
Uranic oxide	0·30
Nickel oxide	0·30
Cobalt sulphate, crystallised.. ..	0·08
	100·00

Glass 248 is similar in composition to the one previously described (197), but is of a darker neutral tint. It is opaque to ultra-violet rays shorter than λ 3550, and cuts off 47 per cent of the heat radiation. It transmits 30 per cent of the incident light. Its tintometer numbers are:—Red, 2·0; yellow, 2·5; blue, 7·5.

Glass 249.

Fused soda flux	88·47
Ferric oxide	1·50
Cobalt sulphate, crystallised.. ..	0·03
Cerium nitrate, crystallised	10·00
	100·00

Glass 249 is of a pale blue tint almost opaque to the ultra-violet rays, the limit of wave-length being λ 3550; to all rays of shorter wave-length it is opaque. It cuts off 51 per cent of the heat radiation, and transmits 63 per cent of the luminous rays. Its tintometer numbers are:—Yellow, 0·5; blue, 2·0.

Glass 250.

Raw soda flux	88·00
Cerium borate	5·00
Ferrous sulphate, crystallised ..	4·15
Uranoso-uranic oxide	2·75
Chromic oxide	0·10
	100·00

Glass 250 has a yellow colour with a faint tinge of green. It cuts off ultra-violet light, being opaque to radiation shorter than λ 3685. It only obstructs 25 per cent of the heat rays, and is transparent to the extent of 74 per cent. In the tintometer the numbers are:—Yellow, 7·00; blue, 1·25.

Glass 251.

Raw soda flux	92·0
Ferrous sulphate, crystallised ..	8·0
	100·00

During the fusion the iron is partially peroxidised. Glass 251 is of a faint yellow colour; it is opaque to ultra-violet rays shorter than λ 3550, it obstructs 37 per cent of the heat radiation, and it transmits 89 per cent of the incident light. Its tintometer number is:—Yellow, 1·25.

Glass 252.

Raw soda flux	72·60
Cerium nitrate, crystallised	24·90
Copper sulphate, crystallised ..	2·10
Nickel oxide	0·40
	100·00

The colour of Glass 252 is faint bluish green. In it copper is introduced to counteract the yellow-brown tint given by the cerium and nickel, and to obtain a tint approaching neutral. It is opaque to ultra-violet rays of shorter wave-length than λ 3680, cuts off 47 per cent of the heat radiation, and transmits 45 per cent of light. The tintometer numbers are:—Yellow, 2·0; blue, 4·5.

Glass 253.

I have already explained that black mica (biotite) is almost perfectly transparent to heat radiation, and at the same time opaque to the luminous rays. I thought it would be interesting to see what would be the effect of melting up some pieces of highly diathermanous biotite with soda flux. After many experiments it was found that a glass of a neutral tint could be made by melting biotite at a high temperature and fusing the result with flux. The proportions are—

Raw soda flux	88·5
Black biotite, fused..	11·5
	100·00

On testing the resulting glass it was found that it had remarkable properties in respect to the heat rays, but in exactly the opposite way to what was expected. It offers

* Read before the Royal Society, November 13, 1913. From the *Philosophical Transactions of the Royal Society*, Series A, vol. ccxiv., pp. 1—25.

n almost complete obstruction to the invisible heat rays, and it cuts off 94 per cent of the heat radiation, and allows 30 per cent of the incident light to pass through. It is opaque to ultra-violet rays of shorter wave-length than λ 3610. It is of a sage-green colour, and its tintometer numbers are:—Yellow, 4·0; and blue, 7·0.

Discussion of the Foregoing Results.

I have already said that the progress of this research has widened since I commenced investigations three years ago. Then my object was to find a glass which would cut off the heat so as to preserve the eyes of those engaged in Glass works. I soon found it difficult, even if it were advisable, to confine the research to the action on heat rays alone. Thus the glasses now described include specimens suitable for spectacles adapted to all requirements—from Eyes of Youth to Eyes of Age.

The first necessity therefore is to find a glass which will cut off as much as possible of the heat radiation. Glass 246—sage-green in colour—is almost perfect in this respect, as it cuts off 98 per cent of the heat. Glass 217—of a pale blue tint—is opaque to 96 per cent of heat radiation. Next comes Glass 253—of a neutral tint—which cuts off 94 per cent; and then come Glass 240—of a neutral tint—cutting off 88 per cent, Glass 210—of a green tint—cutting off 87 per cent heat radiation, and Glass 158—of a pale greenish yellow—cutting off 63 per cent of the heat radiation. If more light is desired to enable the workers to see better at the expense of a little athermancy, Glass 249 is commendable. It is a very pale blue and transmits 63 per cent of luminous rays while cutting off 51 per cent of the heat rays. Spectacles of this glass scarcely appear to obstruct light at all, and the colours of objects are practically unchanged.

For ordinary use, when no special protection against heat radiation is needed, the choice will rest on whether the ultra-violet or the luminous are most to be guarded against; or whether the two together are to be toned down. To begin with I will take into consideration glasses most effective in cutting off ultra-violet rays. Ordinarily the visible spectrum is assumed to end at the Fraunhofer line K, λ 3933, but light can easily be distinguished some distance beyond by the naked eye. For instance, about fifty years ago, with a quartz spectroscope with solar rays, I could see L, λ 3820, and M, λ 3727, though now I cannot see above K. It may therefore be considered that the ultra-violet rays which are to be cut off on account of their probable injurious action are those of shorter wave-lengths than, say, λ 3700. The most effective glasses for this purpose are 158, 150, 240, 246, 202, and 197, all of which are opaque to rays shorter than 3700. The colours are pale green, yellow, and neutral; they transmit ample light so that a choice of tints is available to suit individual taste.

If much transparency is required there is a choice between glasses 187, 150, 251, 250, 247, and 238, which transmit from 99·5 to 70 per cent of the incident light. The choice between this range of glasses will depend on the conditions required, *i.e.*, on the absolute transparency or the colour. The colours are pale tint of yellow, green, and neutral.

If only a moderate degree of transparency is desired Glasses 158, 249, and 221 may be selected; the light transmitted ranges from 70 to 60 per cent, and the tints are of pleasant green, blue, and orange.

When glasses are required which are restful to the eyes in the glare of the sun on chalk cliffs, expanses of snow, or reflected from the sea, Glasses 249, 197, 252, 165, 210, and 248 are most suitable, the tints being yellow, green, and neutral. Moreover, they have the advantage of cutting off practically all the ultra-violet rays and also a considerable amount of the heat radiation.

For convenience of reference all the glasses above described are arranged in the following four tables:—

I. Absorption of Heat Rays.
II. Absorption of Ultra-violet Rays.
III. Transmission of Luminous Rays.
IV. Reduction of Glare.

This latter property is the most valuable for general use in brilliant light.

Table I.—*Absorption of Heat Rays.*

Glass No. 246 cuts off	98	per cent.
217	,,	96
253	,,	94
240	,,	88
210	,,	87
158	,,	63

Table II.—*Absorption of Ultra-violet Rays.*

Glass No. 240. Opaque to rays of shorter w.l. than	3950
202	3830
246	3800
197	3800
158	3700
221	3685
150	3620

Table III.—*Transmission of Luminous Rays.*

Glass No.	187	transmits	99	per cent
,,	251	,,	89	,,
,,	250	,,	74	,,
,,	150	,,	73	,,
,,	247	,,	71	,,
,,	238	,,	71	,,

Table IV.—*Reduction of Glare.*

Glass No.	Absorption of heat. Per cent.	Absorption of ultra-violet.	Transmission of light. Per cent.	Colour.
249	51	3550	63	Pale blue
197	41	3800	45	Pale neutral
252	47	3680	45	Faint blue-green
165	38	3680	42	Pale yellow-green
210	87	3620	30	Blue-green
248	47	3550	30	Dark neutral

THE COMPRESSION AND DENSITY OF RAW MATERIALS USED IN THE MANUFACTURE OF PAPER.

By CLAYTON BEADLE and HENRY P. STEVENS.

Wood, in point of quantity, is the chief source of raw material for the manufacture of paper. Certain countries, like Scandinavia, Russia, Finland, Germany, Canada, United States, are big pulp producing countries, and what they do not require for their own use they export. Other countries, such as Great Britain and parts of the British Empire other than Canada, France, Italy, Spain, Austria, China, and Japan, which are big paper making countries, depend on outside sources of supply of wood-pulp. As supplies for such countries come from long distances over the seas, freight is a matter of great importance The freight is largely determined by bulk, and therefore the question of density, not only of bales of wood-pulp but also other forms of paper making raw materials, is of very great importance. There are several fibres that would be worth while considering as raw materials in the manufacture of paper if it were not for their excessive bulk, which would put such a freight upon them as to render the cost of delivery into this and other importing countries prohibitive, in spite of the fact that such materials may be had for the asking in the localities where they grow. Straw as raw material in the manufacture of pulp and paper has been killed in this way in England. Esparto, which is a somewhat bulky material, has the compensation of cheap back freight from the shores of the Mediterranean.

The question of bulk in the natural state of growth or gathering is of secondary importance, provided that a high

density by compression can be obtained at a reasonable cost. The object of this communication is to show what densities are commercially obtainable with a few of the paper making raw materials.

TABLE A.—*Density Equivalents.*

Cubic feet per ton.	Pounds per cubic foot.	Sp. gr. (water = 1·00).
23·8	93·7	1·500
25	89·6	1·433
30	74·7	1·195
35	64·0	1·024
40	56·0	0·896
45	49·6	0·796
50	44·8	0·717
60	37·3	0·597
70	32·0	0·512
80	28·0	0·448
90	24·9	0·398
100	22·4	0·358
110	20·4	0·326
120	18·7	0·300
130	17·2	0·275
140	16·0	0·256
150	15·0	0·240
200	11·2	0·179
250	9·0	0·143
300	7·5	0·120
350	6·4	0·102
400	5·6	0·090

Table A gives equivalents in cubic feet per ton and pounds per cubic feet, and density or specific gravity (water = 1·00). This table will be found useful for reference when considering the subject generally. As cellulose and vegetable fibres generally, as used or available for use in the manufacture of paper, possesses a specific gravity of 1·500, or a figure very closely approximating thereto, any cellulosic material compressed to its final condition so as to eliminate all air space would have a gravity of 1·500 and would weigh 93·7 lbs. to the cubic foot = 23·8 cubic feet per ton. This figure is inserted at the top of Table A in order to see how nearly highly compressed bales approach to the ultimate condicion of compactness, and by the aid of such figures it is easy to calculate from any density obtained by hydraulic pressing the percentage by volume of air space and fibre. Compression of this order, *i.e.*, approaching the complete elimination of air space, is brought about when paper is highly compressed for coverings of calender bowls, or for structural work as for the interiors of railway waggon wheels; but this compression is never quite to the extent of eliminating the whole of the air space.

In practice, for the baling of raw material to be used in the manufacture of paper, the extent of compression is limited (*a*) by the cost of compression, (*b*) by the condition of the material when compressed, and (*c*) the question of deadweight. Heavy compression within limits can be brought about at a reasonable cost per ton, but the first cost of installation is greatly augmented if high compression is to be resorted to. High compression cannot be done cheaply unless operated on an extensive scale, and the hydraulic presses are heavy, but it is a comparatively easy thing to give a medium compression such as 20 to 25 lbs. per cubic foot, even by hand or horse labour and with comparatively inexpensive light and portable presses. Then, again, the compression must not be carried to the extent of destroying or damaging the paper making qualities of the raw material. High compression with some materials is very detrimental on account of the breaking up of the fibres during the compression. For instance, an excessively high density in the case of esparto would be destructive, and would make it very difficult to conduct the subsequent operations of opening up, dusting, &c., preparatory to boiling. There is a limitation here in the amount of compression, which is of necessity much less than in the case of chemical or mechanical wood pulp; but with cotton-seed cotton, which is discharged direct from the bales into the boiler, high compression such as can be obtained by the most powerful hydraulic presses is, in our opinion, of no detriment provided that the material is sufficiently broken up to ensure the complete penetration and circulation of liquor during the process of boiling. The same may be said of *Hedychium coronarium*, and, as will be hereafter seen, this fibre is capable of very high compression without destroying or impairing its paper making qualities. Table A ranges from completely compressed cellulose materials to materials in a loose unbaled or piled up condition.

The third limitation point in regard to compression, namely, deadweight, must not be lost sight of. Since deadweight comes in at 40 cubic feet per ton (= 56 lbs. per cubic foot), there is no use compressing beyond this point unless it be, perhaps, for land transport and storage in warehouse and factory.

TABLE B.—*Comparative Densities of Different Raw Materials used in the Manufacture of Paper.*

	Cubic feet per ton.	Pounds per cubic foot.
Esparto bales	120	18·7
Do. Hydraulic press	90	24·9
Moist "mechanical" wood-pulp (50 per cent water	44 36	51 61
Do. Mean	40	56
Do. Equivalent dry weight	80	28
Moist "mechanical" wood-pulp (50 per cent water	40/45	56/50
Do. Equivalent dry weight	80/90	28/25
Chemical wood-pulp (sulphite), ordinary compression, air dry	65	34
Best practice for sulphite, air dry	50	45
Chemical wood (soda) kraft, dry	80	28
Chemical wood-pulp (sulphite), dry by measurement and weight of bales in mills	61·6 54	36·4 41·5
Do. Mean	57·8	39
Hedychium coronarium, continuous light baling press	90	25
Do. "Heavy"	64/56	35/40
Do. Heavy hydraulic presses	37/38	60/61
Do. Greatest compression obtained with bales (dry)	33/34	66·0
Do. (Wet)	33/34	66·8

Table B shows a comparison of densities of different paper making materials. It will be noticed that the bulkiest material is esparto. Moist mechanical wood-pulp reaches deadweight, but inasmuch as it contains 50 per cent of water a dry ton has a volume of 80 to 90 cubic feet. Serious attempts have been made in modern pulp mills to compress to 40 per cent of moisture, but it is doubtful whether this will be accomplished economically. There appears to be a greater uniformity of compression in the case of "mechanical" than with "chemical" wood-pulp. This may be due to the fact that in the case of mechanical a definite amount of moisture is aimed at, namely, 50 per cent, and this is regulated by the amount of compression. There is also the important difference that mechanical is pressed moist and chemical compressed dry. "Soda" or sulphate pulp, as might be expected, gives less compression than sulphite; the sheets of sulphite are made compact before baling, but the amount of compression, whether for chemical or mechanical, varies with different mills, according to the power installation and the qualities of the pulp-wood as well as the wood-pulp operated upon. There is a great difference in the qualities of "sulphite" and "soda," one being much harder than the other, and mechanical varies very much in its qualities according to the sources of supply, the mode of grinding, and so forth. The mean results for moist mechanical, taken by us from different sources, show practically the same figures, *i.e.*, 40 cubic feet per moist ton = 56 moist pounds per cubic foot, which

is deadweight. The first figures given for moist mechanical show how the density varies between individual bales, the second figures were arrived at from measurements made in bulk.

Hedychium baling was tested first of all in continuous light baling presses. The *Hedychium* operated upon was in the condition as shipped from Brazil, *i.e.*, after passing through crushing rolls and drying prior to shipping, that is in the form of a loose tow. *Hedychium* as piled or packed loose has a density of about 5 lbs. to the cubic foot. On packing into digesters it will occupy about 10 lbs. per cubic foot. With Howard's Dreadnought heavy continuous presses it gives bales of a density of from 35 to 40 lbs. per cubic foot; with lighter presses of the same type 25 to 30 lbs. per cubic foot. Either the light continuous or heavy Dreadnought presses will bale material at the rate of 20 tons dry weight per diem. For greater densities it is advisable to employ hydraulic pressure. With heavy compressions with hydraulic presses 60 lbs. per cubic foot is obtainable, which is more than is necessary for deadweight. In order to see what was the greatest density obtained with *Hedychium*, pressures of over 1 ton per square inch were employed on small bales at the works of Messrs. Howard and Sons. The highest compression for dry *Hedychium* in the form of bales was 66 dry lbs. per cubic foot. This compression is not detrimental to the qualities of the product. In this condition of baling it can be used for the manufacture of paper, and without these qualities having been impaired as the result of high compression. For moist *Hedychium* we obtained bales containing 66·8 moist lbs. per cubic foot.

Table C.—*Laboratory Baling Tests with Hedychium.*

	Grms. per cc.	Lbs. per cub. ft.
Raw dry Hedychium, pressed in Cider Press—		
Packed before pressing	0·089	4·4
Do. Whilst under pressure	0·355	17·6
Boiled Hedychium, pressed in Cider Press—		
Gross weight (68 per cent moisture)	1·20	75·0
Equivalent dry weight	0·385	24·0
Baling in iron cylinder—		
Raw dry, under pressure	1·24	77·5
Do. Pressure released	1·00	62·5
Raw wet (47 per cent moisture), under pressure. Dry weight	1·00	62·5
Do. Pressure released. Dry weight	0·71	44·4
Ordinary pressing without a "former"—		
Gross weight (55 per cent moisture)	1·00	62·5
Equivalent dry weight	0·45	28·2
Gross weight (42 per cent moisture)	1·20	75·0
Equivalent dry weight	0·695	43·5

Table C gives some experimental baling with *Hedychium* where the density is expressed in grms. per cc. and lbs. per cubic foot. This gives one some idea of the amount of diminution of volume during the process of baling. In practice the reduction in volume is considerable, one ton dry weight uncompressed occupying over 400 cubic feet, after compression less than 40, that is it reduces to about one-tenth. A continuous baling press, by producing bales of a density of 25—30 lbs. to the cubic foot, is well adapted to this work as a first operation. The next operation is best done by compressing two bales into one to a density of 60 lbs. to the cubic foot prior to shipment. The laboratory results obtained with cider presses in light compressions seem to indicate that greater dry weight per cubic foot can be obtained if the material is compressed in a moist rather than a dry condition. This is due to the material becoming more yielding to the pressure when moist than when dry, but when heavier pressures are employed the moisture taken up by the fibre causes it to swell somewhat and to offer a barrier to anything like complete compression, so that the reverse is the case, namely, for high densities the dry goes closer than the moist. Thus 77 lbs. per cubic foot, before releasing from the presses, has been actually obtained in making dry compressions; this expands to 62 lbs. to the cubic foot when the pressure is released, but when the moist material, containing about its own weight of water, is similarly treated in iron cylinders, the density under full compression is 66 and when released 44 dry lbs. per cubic foot. The same is to be noticed when baling under hydraulic pressure recorded in Table B. In the case of the hydraulic pressed bales we obtained 66·0 dry lbs. from the dry pressing and 66·8 moist lbs. per cubic foot from the moist materials after release from press. Unfortunately we did not take note at the time of the dry weight in the wet baling, but we have since dried out the bale and find that it had a density of 38 dry lbs. per cubic foot under equal pressure with the former.

The conclusion is, therefore, that for moderate pressures and density, a greater dry weight per cubic foot is to be obtained baling moist than when baling dry, but that with hydraulic pressure for high densities, *i.e.*, in the neighbourhood of dead weight, the greater dry density is obtained by baling air dry or in the neighbourhood of air dryness.

THE SCIENTIFIC WEEK.

From Our Own Paris Correspondent).

Treatment of Malignant Tumours by the X-Rays.

As is well known the X-rays are now often employed in the treatment of superficial cancerous affections. Concerning this subject a very interesting observation has been made by MM. Reboul and Nogier, and communicated to the Academy of Sciences by M. Roux, director of the Pasteur Institute. These authors have observed that when the X-rays are employed in successive applications in the treatment of malignant tumours, in certain cases the action of these rays grows gradually weaker, and that at a certain moment cancerous elements are no longer reached and affected by the treatment, before a complete cure has been obtained. These decreases of the radiosensibility appear to result from a kind of habit; that is to say, that the cancerous elements grow used to the X-rays, whose effect is thus lessened. The case is not always the same in all the subjects nor in all the cases treated. In order to avoid these inconveniences, MM. Reboul and Nogier advise, whenever the action of the X-rays does not seem to be constant, to take away all that is possible of the tumour before beginning a fresh application of the rays.

Mechanism of the Inactivation of Serums by Dialysis.

In a new technical notice by M. Tissot, communicated to the Academy by Prof. d'Arsonval, the author explains the conditions that govern the dissociation of soaps in serum as well as the mechanism of the inactivation of serums by dialysis, in view of establishing the nature and the constitution of the body that possesses the bacteriological power, that is to say "alexine."

Different Species of Lead.

The interesting hypothesis of the existence of several species of lead results from the researches of M. Maurice Curie concerning the atomic weight of lead of diverse origins. It is known that the radio-active theories, according to which certain bodies, such as radium, uranium, thorium, can evolve and become transformed into other elements, have had a striking confirmation by the transmutation of radium into helium. It is also known that

the same theories lead to the assigning as the ultimate term of the series of these transformations one of the most common metals, that is to say, lead, which thus is derived from the metal that at the present time is by far the dearest (several hundreds of thousand francs a grm.). Continuing his researches undertaken in this direction, M. Maurice Curie, for the atomic weight of lead existing in uraniferous ores, has found the figure of 206·5, whilst the atomic weight of ordinary or galenic lead is 207·01. From this he concludes that there are several varieties of lead of different atomic weights according to the initial metal from which they are derived.

Election of a Perpetual Secretary at the Academy of Sciences.

After a ballot in which 50 members voted, the Academy of Sciences has just elected, by 39 votes, M. Alfred Lacroix, Professor of Mineralogy at the Natural History Museum, as perpetual secretary for physical sciences, in place of the late M. Van Tieghem. The scientific works of M. Alfred Lacroix concern the mineralogy, geology, and physics of the globe. He has studied mineralogy quite as much as a naturalist and as a physicist. In the numerous papers he has published he has especially tried to seek out the mode of the formation of rocks and minerals and their *rôle* in nature, for he does not consider them as simple chemical salts. Instead of working in a laboratory he prefers to pursue his studies on the spot, in the most diverse regions of the world, employing experimentation whenever this was possible. Throughout all the scientific researches of Prof. Lacroix the same general directing idea, the same plan is to be found. When he studies the determination of properties, and in particular of the optical properties of minerals, he searches what are their variations, with the conditions of their layers and their mode of formation. He applies the data thus obtained to the determination of the composition of rocks and searches the origin of metamorphic rocks and those of the eruptive rocks which have produced them. His "Mineralogy of France and Her Colonies," his memoirs on metamorphism, his observations on the eruptions of Martinique, of Vesuvius, of Etna, of the volcanos of the Réunion are the principal steps of his scientific researches. Born at Macon in 1863, M. Lacroix was appointed assistant at the Collège of France in 1887, Doctor of Science in 1889, Professor of Mineralogy at the Natural History Museum in 1893; he became a member of the Academy of Sciences in 1904. He is a member of most of the different foreign scientific academies throughout the world, and has been charged with no less than fourteen scientific missions in nearly all the countries of the globe. As head of the mission of Mont Pelée in 1902, Prof. Lacroix created the Martinique Observatory, where he made some very fine researches on the eruptions of Mont Pelée. He contributed fresh information as to the formation of the domes raised by volcanic rocks, and also concerning a little known phenomenon, that of "*nuées ardentes*." These clouds of *nuées* were veritable agents of destruction and death, which clased the eruption of Mont Pelée among the most homicidal that history has ever had to enregister. M. Lacroix was able to study, near at hand, seventeen eruptions of these thick clouds. He has seen them roll like a liquid on the surface of the soil. Their temperature at a distance of 6 kilometres from their point of departure was 200°. At this same time, the eminent mineralogist studied the volcano of Saint-Vincent and the sulphur mine of Guadeloupe. Lastly, the geological study that he has made of the large African island of Madagascar is one of the most important works of Prof. Lacroix.

King's College.—Professor Herbert Jackson, of King's College, has been appointed Head of the Chemical Department of the College, with the title of Daniell Professor of Chemistry in the University of London.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, June 4, 1914.

Prof. W. H. Perkin, LL.D., F.R.S., President, n the Chair.

The President referred to the loss sustained by the Society through the death of Sir Joseph Wilson Swan (elected, June 3, 1865; died, May 27, 1914).

Mr. D. R. Keller was formally admitted a Fellow of the Chemical Society.

A certificate was read for the first time in favour of Mr. George von Kaufmann, jun., Christ's College, Cambridge.

Of the following papers, those marked * were read:—

*153. "*The Influence of Nitro-groups on the Reactivity of Substituents in the Benzene Nucleus.*" By James Kenner. (This paper was read at the meeting on May 21, 1914).

The influence mentioned in the title was referred to two distinct functions exercised by nitro-groups. One of these, which is shared with other meta-directive groupings, consists in the conferment of a certain degree of mobility on substituents in ortho- or para-positions, and was explained in terms of Flürscheim's views. The other enables the substituent, thus rendered mobile, to take part in reactions, in spite of the steric influences to which it is exposed. This function is exercised most powerfully by the nitro-group, and was correlated with another property characteristic of nitro-groups, namely, the power to form additive compounds.

An alternative theory, proposed by Borsche (*Annalen*, 1911, ccclxxxvi., 356; 1913, cdii., 81) was also discussed.

With the assistance of Mr. R. Curtis, and in connection with the views developed above, the action of hydrazine hydrate on methyl 2-chloro-3:5-dinitrobenzoate was studied and shown to lead at once to the formation of 5:7-*dinitro*-3-*keto*-1:3-*dihydroindazole*, without admitting of the isolation of the intermediate hydrazine derivative. In the case of phenylhydrazine, the main product was 5:7-*dinitro*-3-*keto*-2-*phenyl*-1:3-*dihydroindazole*, accompanied by a small proportion of 2:4-*dinitro*-6-*carbomethyoxyhydrazobenzene*, and another compound of unknown constitution.

The indazole derivatives named gave rise to quinonoid *sodium* salts, whilst, by the action of phosphoryl chloride at 180°, 3:5:7-*trichloroindazole* and 3:5:7-*trichloro*-2-*phenylindazole* were produced, the nitro-groups attached to the benzene nucleus having suffered displacement by chlorine atoms.

Discussion.

Dr. Flürscheim welcomed Dr. Kenner's paper as an interesting contribution on the problem of benzene substitution. It appeared that, generally, chemical reactivity was governed by the nature of the affinity of the atoms involved (polar factor), by the amount of that affinity (quantitative factor), and by considerations of space (steric factor). Dr. Kenner had taken the last two factors into consideration, and he had been able to embrace a considerable number of facts. At the same time the polar factor could, of course, not always be neglected. For the mobility, for instance, of a nitro-group in 1:3:5-trinitrobenzene (Lobry de Bruyn), of fluorine in *m*-fluoronitrobenzene (Holleman), or of the 1-bromine in 1:2:4:6-tetrabromobenzene (Jackson and Calvert), it even appeared that the polar factor was alone responsible; in other words, even when a sufficient *amount* of affinity was available for it, a substituent might easily be detached from the nucleus when both exhibited strong electropolarity of the same kind, so that the *nature* of their affinity was not conducive to mutual saturation (compare *Ber.*, 1906, xxxix., 2016). Undoubtedly, the problem of the replacement of one

benzene substituent by another was more complex than that of the mere substitution of hydrogen, and he was glad that Dr. Kenner had brought the subject before the meeting.

Prof. J. T. Hewitt referred to the work of Borsche and Babr (*Annalen*, 1913, cdii., 81), which shows that in the apparently symmetrical 4 : 6 dichloro-1 : 3-dinitrobenzene, one halogen atom is more mobile than the other. This might be explained if the products with amines, &c., assumed a quinonoid configuration; for if the 6-chlorine atom had reacted, and quinonoid structure were established between positions 6 and 1, the linking between the carbon atoms 3 and 4 must of necessity be a single one.

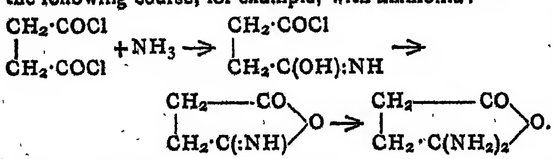
Dr. Kenner agreed that his views might need amplification in order to become applicable to all the observed cases of mobility, and cited, as an example, the formation of the trichloroindazoles mentioned above. In his opinion, recent work on the metallic ketyls lent strong support to the view that colour was connected with the presence of residual affinity, and therefore to Hantzsch's formula for the nitroanilines. He drew attention to another apparent fallacy in the views expressed by Borsche and Bahr, and suggested an alternative explanation of the results obtained by these workers.

*154. "*Studies in the Succinic Acid Series.* Part I. *The Chlorides of Succinic and Methylsuccinic Acids, and their Constitution.*" By George Francis Morrell.

Since succinyl chloride gave with ammonia a 90 per cent yield of *as*-succinamide, and with benzene and aluminium chloride a similar amount of succinophenone, Auger (*Ann. Chim. Phys.*, 1891, [4], xxii., 326) concluded that it was a mixture of two isomerides. Meyer and Marx (*Ber.*, 1908, xli., 2459) found that it gave with alcohols only the normal esters, and suggested a theory of tautomerism. In the present investigation, succinyl and methylsuccinyl chlorides have been prepared, and a consideration of their physical properties and anomalous behaviour with ammonia and substituted ammonias is held to disprove Auger's theory, and to lend no support to the tautomerism theory. Succinyl chloride, for example, was found to be a crystalline solid, melting sharply at +20°, and boiling at 87—88°/18 mm. Whether the first or last portions of the distillate were taken, it gave with aniline nothing but the *s*-anilide (m. p. 230°); with methylamine, only a 15 per cent yield of the *s*-dimethylamide; and with ammonia almost entirely the *as*-amide.

It is concluded that these acid chlorides are definite chemical individuals, and that there is no satisfactory evidence whatever for assigning to them any other constitution than that of normal acid chlorides, $COCl{\cdot}CH_2{\cdot}CH_2{\cdot}COCl$.

The formation of asymmetric products probably takes the following course, for example, with ammonia:—



*155. "*The Dilution Limits of Inflammability of Gaseous Mixtures.* Part I. *The Determination of Dilution Limits.* Part II. *The Lower Limits for Hydrogen, Methane, and Carbon Monoxide in Air.*" By Hubert Frank Coward and Frank Brinsley.

The smallest amount of hydrogen in an inflammable mixture of hydrogen and air has been variously stated as low as 4·5 and as high as 10 per cent. Similarly, the values given for the greatest amount of hydrogen in an inflammable mixture of hydrogen and air are as low as 55 per cent and as high as 80 per cent. The hydrogen-oxygen mixtures show similar want of accord in the results of previous workers. A partial explanation exists in Clowes's observation that in certain weak mixtures a flame may be propagated upwards, but not downwards.

A re-examination of the inflammability of weak gaseous mixtures has been started, based on the definition that a mixture at a defined temperature and pressure is inflammable *per se* if, and only if, it will propagate flame indefinitely, the temperature and pressure of the unburnt gases being constant. The flame observed in many weak mixtures travels more slowly than the convection current set up by the flame, so that the criterion of inflammability is the observed travel of a flame upwards through a vertical vessel of sufficiently great dimensions to avoid appreciable cooling influence by the walls and to provide a sufficient length for observation of the flame to leave no doubt as to its capacity for indefinite self-propagation.

The experiments of previous observers do not satisfy this criterion, and the critical experiments of the authors have been carried out in vessels, one having a capacity of 170 litres, another a length of 4·5 metres. With all three gases used, the flames in certain weak mixtures have been observed to start as vortex rings, which rose, expanded, and ultimately broke into a general self-propagating inflammation, or were extinguished. The lower limits of inflammability of mixtures of each of the three gases with air saturated with aqueous vapour at 17° to 18° were:—

Hydrogen	4·1 per cent
Methane	5·3 "
Carbon monoxide	12·5 "

Discussion.

Prof. Bone drew attention to the great importance of accurate information concerning the behaviour of gaseous mixtures at or near the lower explosion limits, and congratulated the authors on both their experimental demonstration and the beautiful photographs which they had exhibited. He agreed in principle with the authors' definition of "inflammability," but pointed out the necessity of distinguishing between "ignitability" and inflammability." The phenomenon of ignition was very complicated, and was probably not a purely thermal one, as Prof. W. M. Thornton had recently shown in an important communication to the Royal Society on the electrical ignition of gaseous mixtures, from which it appeared probable that ionisation was a factor precedent to the actual combustion.

Dr. Scott suggested that the mixtures of hydrogen with oxygen and with air might be made more luminous by using weighed quantities of sodium, which would give the required quantities of hydrogen in contact with the water. The brilliant yellow of the flame would probably enable much more detail to be visible to the eye and to be recorded on the photographic plate.

Dr. E. Rideal asked whether there was any indication of a dark wave preceding the luminous cap which travelled up the tube.

The dark wave caused by local compression of the gas could be conveniently photographed by a method which he had used with great success in the case of rifle bullets travelling through different gases. The bullet in its course is made to traverse two copper gauze disks placed close to one another; by this means contact is made between the two disks, which are connected to the outsides of the Leyden jars of a Wimshurst machine. The primary spark follows a short time after contact is made, and if there is a photographic plate opposite to the spark-gap of the Wimshurst, the bullet, passing between the spark and the plate, throws its shadow on the latter. In front of the photograph of the bullet is always observable a parabolic-like curve, being a cross-section of the paraboloid-shaped mass of compressed air partly dragged and partly pushed forward by the bullet in its flight. The line on the plate is caused by the fact that the compressed air has a different refractive index to that surrounding it. Different gases gave curves of the same order, but different constants. In the present case, during combustion one might expect local differences of pressure, indications of which could be obtained by an adaptation of the foregoing method.

Dr. Coward agreed with Prof. Bone that it was desi-

able to distinguish between inflammability and ignitability. A large flame might be developed in a mixture when an electric spark was passed or a jet of flame introduced into it, although the inflammation would not be capable of indefinite self-propagation. This mixture would therefore not be inflammable *per se*, but a possibly dangerous flame might be formed in it; the initial impetus of the spark was not rapidly dissipated. The authors had seen such flames in mixtures just below the dilution limit which were nearly 30 cm. wide, and travelled 60, 90, or even 120 cm. from their source.

Dr. Scott's suggestion for rendering the hydrogen flames more luminous would be useful for photographic purposes; up to the present, the authors had desired to see and record the appearance of flame in pure mixtures, and for that reason to avoid the presence of spray or dust particles.

*156. "*The Thermal Decomposition of Methyl Alcohol.*" By WILLIAM ARTHUR BONE and HAMILTON DAVIES.

The authors find that methyl alcohol vapour decomposes on heating principally in two ways, namely:—

1. An essentially low-temperature decomposition into, primarily, steam and a residue, $:CH_2$, which has a fugitive free existence, $CH_3{\cdot}OH = :CH_2 + H_2O$.

2. The normal high-temperature decomposition primarily into formaldehyde and hydrogen, the formaldehyde then decomposing into carbon monoxide and hydrogen,—

$$CH_3{\cdot}OH = \overbrace{CH_2O}^{CO+H_2} + H_2.$$

Thus, at 650°, 20 to 25 per cent of the methyl alcohol decomposes according to (1), the remainder according to (2), the $H_2C:$ formed during (1) combining with part of the H_2 produced during (2), forming methane.

At 1000°, more than 95 per cent of the methyl alcohol decomposes according to (2), the remainder according to (1).

At neither temperature is there any separation of carbon, nor could any acetylene be detected in the products.

157. "*A Comparative Study of the Absorption Spectra of some Compounds of Phosphorus, Arsenic, Antimony, and Bismuth.*" (Preliminary Note). By CECIL REGINALD CRYMBLE.

In accordance with the rule connecting valency and absorption (*Trans.*. 1912, ci., 266), it has been found that solutions of compounds of the above elements absorb ultra-violet light, the extent of the absorption varying greatly with the nature of the compound.

If the chlorides ECl_3 are compared, the limit of general absorption is displaced towards the visible on passing from phosphorus chloride to bismuth trichloride, and in the latter compound an absorption band makes its appearance in Bi/1000 solution with a head at 2850.

The pentachlorides of phosphorus and antimony have been examined, and they possess much greater absorptive power than the corresponding trichlorides. The limit of the general absorption of antimony trichloride and the absorption band of bismuth chloride are displaced towards the visible on formation of the complex salts $ECl_3,nMCl$.

Like sulphates and selenates, the highly oxidised phosphates and arsenates are quite diactinic; antimonates and arsenites show slight absorption; and, as is known, bismuthic acid is a red powder.

The grouping P:O in the phosphorus oxy-acids is devoid of absorptive power, and phosphoryl chloride is almost diactinic.

The investigations are being extended to the fourth group of elements, especially to tin and lead; and from the variations in the absorptive power of solutions of stannic chloride, which occur on keeping, it is hoped to gain some information on the constitution of these salts.

158. "*The Reactions of* α-*Amino*-β-*hydroxy-compounds as Cyclic Structures.*" By JAMES COLQUHOUN IRVINE and ALEXANDER WALKER FYFE.

The behaviour of β-hydroxy-αβ-diphenylethylamine towards methylating agents has been studied in order to ascertain if compounds in which a secondary hydroxyl group and a primary amino-group are attached to neighbouring carbon atoms are capable of reacting in accordance with a cyclic formula. By the action of silver oxide and methyl iodide on the amine, a dimethyl derivative melting at 135—137° was obtained. As this compound contained no normal methoxyl group, yet nevertheless failed to form a methiodide, a hydrochloride, or a platinichloride, it is regarded as the *anhydride of* β-*hydroxy*-αβ-*diphenylethyldimethylammonium hydroxide* (I.). In the absence of salt forming properties, and in its capacity to combine with silver iodide, the compound resembles the alkyl glucosamines, for which a cyclic structure has already been suggested.

On the other hand, direct methylation of β-hydroxy-αβ-diphenylethylamine by means of methyl iodide gave successively β-*hydroxy*-αβ-*diphenylethylmethylamine*, β-*hydroxy*-αβ-*diphenylethyldimethylamine* (II.), and the corresponding *methiodide*. The properties of these substituted amines are perfectly regular in that they form salts and platinichlorides, from which it may be concluded that the normal open-chain structure may be applied to them. The following formulæ are consequently ascribed to the isomeric compounds isolated:—

(I.)	(II.)
$C_6H_5{\cdot}CH{\cdot}O$	$C_6H_5{\cdot}CH{\cdot}OH$
$C_6H_5{\cdot}CH{\cdot}NHMe_2$	$C_6H_5{\cdot}CH{\cdot}NMe_2$

The constitution assigned to β-hydroxy-αβ-diphenylethyldimethylamine (II.) was confirmed by the conversion of the compound into β-*methoxy*-αβ-*diphenylethyldimethylamine*, $OMe{\cdot}CHPh{\cdot}CHPh{\cdot}NMe_2$, which, in turn, reacted with nitrous acid to give hydrobenzoin methyl ether. The same methoxy-amine resulted from the methylation of β-*methoxy*-αβ-*diphenylethylamine*, both by the silver oxide reaction and by the agency of methyl iodide, the compound in the former case being isolated as the *methiodide* combined with one molecule of silver iodide.

The results of the investigation are applied to the constitution of the alkyl glucosamines, and the capacity of these compounds to combine simultaneously with alkyl haloids and with silver haloids is explained on the assumption that the addition takes place through the oxygen atom of the ring.

159. "*Ionic Equilibria Across Semi-permeable Membranes.*" By FREDERICK GEORGE DONNAN and ARTHUR JOHN ALLMAND.

Experiments have been made on the distribution of potassium chloride between two compartments separated by a copper ferrocyanide membrane, one compartment containing potassium ferrocyanide. The higher concentration of potassium chloride in the solution free from ferrocyanide, and the quantitative relation of this unequal distribution to the concentration of chloride and ferrocyanide, have been established.

The results agree, in general, with the view of such membrane-equilibria proposed by Donnan. A discussion of the distribution data and the measurements of electromotive force appears to show that, at all events in the case of a copper ferrocyanide membrane and potassium ferrocyanide solutions, the phenomena are quantitatively not so simple as supposed in the theory mentioned.

160. "*The Effect of Ring-formation on Viscosity.*" By FERDINAND BERNARD THOLE.

The opinion previously put forward that ring-formation is accompanied by an increase in viscosity has been confirmed by a comparison of the viscosities of a considerable number of cyclic compounds (carbocyclic and heterocyclic rings containing from two to seven atoms) with those of corresponding open-chain analogues. The chemical types of the latter have been carefully chosen to correspond with those of the cyclic compounds, since the results of some previous investigators with other physical properties have been confused by illegimitate comparisons.

Viscosity has been found to fall in line with certain other physical properties in showing an anomaly which varies steadily as the complexity of the ring increases, and giving no change of direction on passing the five-membered ring-system.

161. "*Action of Monochloracetic Acid on Thiocarbamide and Monoalkylated Thiocarbamides.*" By Prafulla Chandra Ray and Francis V. Fernandes.

By the action of monochloroacetic acid on thiocarbamide in aqueous solution, the latter evidently tautomerises, and gives rise to *formamidinethiolactic acid*, $NH_2{\cdot}C(:NH){\cdot}S{\cdot}CH_2{\cdot}CO_2H$. If, however, acetone is used as a solvent, the corresponding hydrochloride of the base is obtained. Similar hydrochlorides are yielded by the action of monochloro acetic acid on mono-substituted thiocarbamides in acetone solution; thus, the hydrochlorides of *methylformamidine-* and *allylformamidine-thiolacetic acids* have been prepared.

162. "*Action of Grignard Reagents on Acid Amides.*" By Alex. McKenzie, Geoffrey Martin, and Harold Gordon Rule.

In continuation of former work (McKenzie and Wren, *Trans.*, 1908, xciii., 310; xcvii., 473; Wren, *Trans.*, 1909, xcv., 1583, 1593), the authors have examined the action of Grignard reagents on several acid amides. In those cases where a ketol was isolated as one of the products, the yield was small. A mixture of benzoin and $\alpha\beta$-dihydroxy-$\alpha\beta\beta$-triphenylethane is produced by the action of magnesium phenyl bromide on mandelopiperidide. The formation of benzoylbenzylcarbinol from α-hydroxy-β-phenylpropionamide is accompanied by the formation of $\alpha\beta$-dihydroxy-$\alpha\alpha\gamma$-triphenylpropane.

d-Benzoylbenzylcarbinol undergoes racemisation at the ordinary temperature when a few drops of sodium ethoxide are added to its alcoholic solution. This change is, however, much slower than that undergone by *l*-benzoin under similar conditions; the value for the rotation of a 5 per cent solution falls to about one-half of the original after 481 hours have elapsed.

163. "*Synthetic Hydrocarbons Allied to the Terpenes.*" By Walter Norman Haworth and Alexander Walker Fyfe.

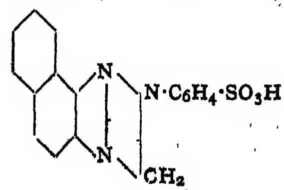
The method used by Blaise (*Comptes Rendus*, 1901, cxxxiii., 1217) for the production of ketones from nitriles has been applied in the synthesis of three hydroaromatic ketones of the *cyclo*hexene series. These were converted into optically active and inactive carbinols and hydrocarbons analogous to the members of the terpene group. The alteration in the rotation values due to the synthetic changes has been carefully studied, as have also the spectrochemical properties. The compounds described are interesting examples of "multiple disturbance" of conjugation, and show the expected diminution of exaltation in accordance with the views of Auwers and Eisenlohr.

164. "*Asymmetric Tervalent Nitrogen.*" (Preliminary Note). By Tom Sidney Moore.

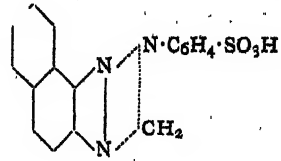
The cause of the failure of the attempts that have been made to obtain optically active compounds owing their asymmetry to the presence of tervalent nitrogen atoms attached to three different groups is probably the rapid racemisation of the substances investigated, which have all been of the type $N\begin{matrix}\diagup a \\ -b \\ \diagdown c\end{matrix}$.

Compounds of the type $N\begin{matrix}\diagup a \diagdown \\ -b- \\ \diagdown c \diagup\end{matrix}N$ and $N\begin{matrix}\diagup a \diagdown \\ --- \\ \diagdown b \diagup\end{matrix}N$, in which *a*, *b*, and *c* are three different divalent groups or chains, of which at least one is unsymmetrical with regard to the two nitrogen atoms, should exist in two enantiomorphic forms. Racemisation might be expected to be slow, or even non-existent, in compounds of the first type, and it might be slow enough in compounds of the second type to allow of the demonstration of isomerism. Experiments on the preparation of suitable compounds of the first type are now in progress; of the second type several examples are known, and one of these has been examined.

The compound chosen was 2-p-*sulphophenyl*-2 : 3-*dihydro*-1 : 2 : 4-*naphtha*iso*triazine*, which was prepared according to the general method given by Meldola and Forster (*Trans.*, 1891, lix., 678), and found to be very similar in properties to the phenyl derivatives described by them. The two possible forms would be:—



and—



The following results were obtained with a specimen of the brucine salt of this compound after it had been twice re-crystallised from alcohol:—

1. The brucine salt was treated at 0° with excess of N-sodium hydroxide, and the resulting aqueous solution extracted with chloroform until it was free from brucine (three extractions). In four such experiments the resulting alkaline solution of the sodium salt showed a small but definite dextrorotation, which decayed with time, until after a few hours the solution was optically inactive. The values for the initial specific rotation of the sodium salt were between + [3·5°] and + [1·7°]. Parallel experiments with the acid itself gave, as one expected, inactive solutions. In other experiments with the brucine salt, where only the equivalent quantity of sodium hydroxide was used, the solution of the sodium salt was inactive; this agrees with the experience of Mills and Bain (*Trans.*, 1910, xcvii., 1866; 1914, cv., 64), who found that excess of alkali hindered the racemisation of their compounds.

2. The brucine salt, when added to chloroform, first dissolves completely, and then deposits some of the acid, this process not being complete for some hours. One such solution was allowed to remain overnight, and its rotatory power was measured after filtration. It was then kept for three days in a closed vessel (during which period no further acid was deposited), and its rotatory power again measured. The angles observed were −0·15° and −0·22° respectively. This change of rotatory power with time indicates that the brucine salt contained an excess of the dextro-acid, which racemised gradually on keeping.

Mr. J. J. Manley very kindly estimated the sulphur in a specimen of the acid recovered from the brucine salt.

Found, S = 9·65. $C_{17}H_{13}O_3N_3S$ requires S = 9·44 per cent.

The author is proceeding with a detailed examination of this and similar compounds; in the meantime, the results given above offer definite evidence of asymmetry in tervalent nitrogen atoms attached to three separate groups.

165. "*The Alkaloids of* Daphnandra micrantha." By Frank Lee Pyman.

The alkaloids of the bark of the Queensland plant, *Daphnandra micrantha*, Benth., have been investigated, and three new crystalline bases, *daphnandrine*, $C_{36}H_{38}O_6N_2$, *daphnoline*, $C_{34}H_{34}O_6N_2$ (or $C_{35}H_{36}O_6N_2$), and *micranthine*, $C_{36}H_{32}O_6N_2$, have been isolated and characterised.

166. "*The Relation between the Absorption Spectra and the Constitution of certain* iso*Quinoline Alkaloids and of the Alkaloids of Ipecacuanha.*" By JAMES JOHNSTON DOBBIE and JOHN JACOB FOX.

It was shown that certain *iso*quinoline alkaloids including tetrahydroberberine, laudanosine, corydaline, the salts of cryptopine and protopine, which possess similar spectra, are all characterised by the presence of unreduced nuclei derived from catechol. When the spectra of one molecule of these alkaloids are compared with the spectra of two molecules of creosol (4-hydroxy-3-methoxytoluene), they are seen to have their band in the same position. In these, as in cases previously described (*Trans.*, 1911, xcix., 1254; 1912, ci., 77; 1913, ciii., 1193), the reduced part of the molecule has very little influence on the spectrum.

It was also shown that the band of the spectrum of morphine, which contains one catechol nucleus, only differs from that of creosol in being somewhat narrower.

Emetine and cephaeline give the same spectrum as the above-mentioned alkaloids, and therefore in all probability also contain catechol nuclei, a conclusion which is in harmony with the facts of their constitution, so far as these are known (Carr and Pyman, *Proc.*, 1913, xxix., 226; 1914, xxx., 157).

167. "*The Interaction of Benzoin and the Chlorides of Dibasic Acids.*" By HAMILTON MCCOMBIE and OHN WILFRID PARKES.

The interaction of benzoin and dibasic acid chlorides was studied in the hope of obtaining compounds derived from one molecule of benzoin and one molecule of the acid chloride, which would prove to be derivatives of stilbenediol. The following acid chlorides were employed:—Carbonyl chloride, oxalyl chloride, phthalyl chloride, and camphoryl chloride. In all cases, however, even when excess of benzoin was employed, the only compounds that could be isolated were formed from two molecular proportions of benzoin and one of the acid chloride. In the case of oxalyl chloride, two different compounds were isolated, both possesing the formula $C_{30}H_{22}O_6$.

168. "*The Fractional Distillation of Petroleum.*" By JAMES MCCONNELL SANDERS.

In the examination of crude petroleum, burning oil, or petrol by the distillation test, it is often desirable to determine the specific gravity of successive fractions; the rule of the New York Produce Exchange requires, for an oil to be considered as a "pure natural oil," that it should exhibit a regular gradation in the densities of successive fractions.

When the Engler method is used for fractionating an oil, or when the amount of sample available is small, the ordinary rapid methods of determining the specific gravities of the fractions cannot be conveniently used. The author described an apparatus whereby the gravity of successive fractions may be determined rapidly during the distillation, the fractions being removed in succession or mixed, and the gradual change of density determined as the distillation proceeds. From the data obtained, curves may be plotted showing the behaviour of an oil during close fractionation, or the effect of cracking at any stage.

Some special difficulties found in the distillation of heavy asphaltic oils of Mexican origin were discussed, more especially in regard to the determination of water and the carrying of the distillation to the "coking stage."

A special distillation flask was described, whereby these difficulties are overcome by means of an electrically deposited copper coating to the flask, an electrically heated and controlled still-head, and the subsequent removal of adhering water in the side-neck and condenser tubes by means of absolute alcohol, which is then treated with magnesium amalgam and the evolved hydrogen measured.

169. "*Mercuration of Aromatic Amines.*" (Preliminary Note). By GILBERT T. MORGAN and J. CAMPBELL ELLIOTT.

The circumstance that aromatic compounds containing metallic and metalloidal substituents are becoming increasingly important in therapeutics renders the conditions of formation of these products a matter of considerable interest. The introduction into aromatic nuclei of arsenic, antimony, and similar metalloids involves reactions needing special precautions, and proceeding only slowly to completion. On the contrary, the mercuration of aromatic amines proceeds so rapidly and quantitatively that the process can be readily demonstrated as a lecture experiment. One grm. of aniline is added to 6·6 grms. of mercuric acetate dissolved in 300 cc. of cold methyl alcohol, and the solution boiled for two minutes. Another 6·6 grms. of mercuric acetate dissolved in 300 cc. of methyl alcohol are boiled for the same time, and serve for a control experiment. The two hot solutions are each poured into 300 cc. of water containing 7·5 grms. of potassium iodide. The control solution of mercuric acetate gives immediately yellow mercuric iodide, changing almost instantaneously into the stable red modification. The solution to which the aniline has been added no longer contains mercuric ions, the whole of the mercury having become attached to the aromatic nucleus. It yields a yellowish white precipitate of di- and tri-iodomercurianilines, which is quite distinct from the red precipitate obtained in the control experiment. *m*-Toluidine (1·1 grm.) may be substituted for aniline in the foregoing experiment, with a similar result, the yellowish white precipitate containing a mixture of di- and tri-iodomercuri *m*-toluidines (compare Schrauth and Schoeller, *Ber.*, 1912, xlv., 2808).

Other bases containing unsubstituted ortho- and para-positions behave in a similar manner. With methylaniline and dimethylaniline, similar proportions (2—3 molecules) of mercuric acetate are taken up, but the resulting yellowish white organic mercuri-iodides are discoloured by red and green oxidation products respectively. An analogous reaction occurs with diethylaniline, the amount of coloured by-product being less. Diphenylamine reacts with 5 6 molecular proportions of mercuric acetate, and yields a voluminous white organo-mercuri-iodide. Aromatic bases, partly substituted in their reactive ortho- and para-positions, are also readily mercurated, but the amount of mercuric acetate taken up diminishes as substitution increases. *o*-Toluidine and dimethyl-*o*-toluidine condense with two molecular proportions of mercuric acetate, and give white organo-mercuric iodides, but with the latter base the reaction proceeds very slowly. *p*-Toluidine reacts readily with 1 molecular proportion of mercuric acetate. Further treatment with more acetate leads to oxidation. Methyl-*p*-toluidine and dimethyl-*p*-toluidine behave similarly.

α-Naphthylamine and β-naphthylamine condense, respectively, with one and two molecular proportions of mercuric acetate, and yield the corresponding organo-mercuric iodides (compare Brieger and Schulemann, *Journ. Pr. Chem.*, 1914, [2], lxxxix., 97).

When the foregoing organo-mercuric iodides are left in contact with hydriodic acid, some of the organically combined mercury is removed in the form of mercuric iodide, but these compounds are not affected by neutral iodides.

170. "*The Viscosities of Mixtures of Formamide with the Alcohols.*" By SOLOMON ENGLISH and WILLIAM ERNEST STEPHEN TURNER.

In confirmation and extension of previous work (Merry and Turner, *Trans.*, 1914, cv., 748), the viscosities of mixtures of formamide with *n*-propyl, *iso*butyl, and *iso*amyl alcohols at 25° have been measured. It had previously been shown that with water, methyl alcohol, and ethyl alcohol, the negative deviation of the observed from the calculated viscosity grew less in the order of the substances named, and it was now shown that the deviation becomes positive with *n*-propyl alcohol, although the viscosity curve does not attain a maximum, and that the *iso*butyl and *iso*amyl alcohol curves each contains a maximum point. The *n*-propyl alcohol curve is sinuous, and the sinuosity is developed in the two higher alcohols, so that they contain,

not only a pronounced maximum, but also a minimum, point.

171. "*Action of Nitro-substituted Aryl Haloids on Alkali Thiosulphates and Selenosulphates.*" By Douglas Frank Twiss.

Various investigations have already shown that the alkyl haloids can react with the alkali thiosulphates, giving the corresponding alkali alkyl thiosulphates; but the few corresponding aryl thiosulphates discovered hitherto have been prepared by less simple processes, usually depending on oxidation of a mixture of sodium thiosulphate and an aromatic substance.

Unsubstituted aryl haloids fail to react with sodium thiosulphate, but the 2:4-dinitro- and 2:4:6-trinitrophenyl haloids readily enter into action with not more than a semimolecular proportion of sodium thiosulphate, yielding, not the corresponding organic thiosulphate compounds, which appear to be capable of only transient existence, but the corresponding sulphides. In a similar manner, reaction with not more than a semimolecular proportion of potassium selenosulphate produces the corresponding selenides.

When an excess of sodium thiosulphate is used with 4-chloro- or 4-bromo-1:3-dinitrobenzene, the resulting 2:4-dinitrophenyl sulphide is not the only product, for the solution subsequently deposits 2:4-dinitrophenyl disulphide. An excess of potassium selenosulphate yields almost exclusively 2:4-dinitrophenyl diselenide.

These results are explained by the primary formation of an unstable alkali aryl thiosulphate or selenosulphate which, in the presence of excess of aryl haloid, passes into the corresponding sulphide or selenide, according to the equation (for the former case)—

$$NaRS_2O_3 + RHal + H_2O = NaHal + R_2S + H_2SO_4,$$

whilst with an excess of inorganic thiosulphate or selenosulphate the alkali aryl thiosulphate or selenosulphate produced subsequently decomposes, as their aliphatic analogues readily do, yielding disulphide or diselenide.

PHYSICAL SOCIETY.

Ordinary Meeting, June 12, 1914.

Prof. T. Mather, F.R.S., Vice-President, in the Chair.

A paper entitled "*Note on the Connection between the Method of Least Squares and the Fourier Method of Calculating the Coefficients of a Trigonometrical Series to Represent a given Function or Series of Observations,*" by Prof. C. H. Lees, F.R.S., was taken as read in the absence of the author.

In view of the number of alternative methods which have been suggested for calculating the coefficients of the terms of a Fourier series to represent a number of observations of a variable quantity, the author points out that the Fourier method gives the most probable values of the coefficients, since it makes the sum of the squares of the errors at the points of observation a minimum.

Discussion.

Dr. C. Chree mentioned that the method was dealt with in Tait's "Natural Philosophy," but no proof was given. Prof. Lees had supplied the proof, and the paper was of interest on that account.

Dr. W. Wilson (communicated remarks) said Prof. Lees deals with a function $f(x)$ of period l, whose values are given in the whole interval from 0 to l. In this case the validity and *uniqueness* of the Fourier expansion (provided $f(x)$ is subject to certain restrictions) have been demonstrated with complete rigour (Dirichlet, "Collected Works," vol. i., pp. 133—160, and G. Cantor, *Journal für Mathematik*, lxxii.). It seems to me therefore that there is no question of the reliability of the Fourier coefficients, and the fact that the method of least squares leads to the usual Fourier expressions for the coefficients confirms the reliability of this method rather than that of the Fourier coefficients themselves.

A paper entitled "*A Magnetograph for Measuring Variations in the Horizontal Intensity of the Earth's Magnetic Field*" was read by Mr. F. E. Smith.

In the case of unifilar instruments for recording variations in H, if θ is the angle which the magnetic system makes with the magnetic meridian, M the moment of the magnet, and H the horizontal intensity of the earth's field, equilibrium results when MH sin $\theta = T\phi$, where ϕ is the torsion on the fibre and T is a constant. In the instrument described ϕ may be made great or small, but high sensitiveness is secured by making ϕ great. The magnet system is supported by a quartz fibre, and critically aperiodic damping is obtained by means of an aluminium vane and two parallel damping plates. To diminish the sensitiveness the effective length of the fibre may be reduced. The general usefulness of the instrument is illustrated by photographic records, which show the instrumental peculiarities to be very small, and indicate that unless the system is aperiodic increased difficulty must result in the interpretation of the records. An overdamped system responds but slightly to rapid pulsations in H, but follows the slow changes which are common all over the world. The general sensitiveness of the records is about 3 mm. for a change in H of 0·00001 C.G.S. unit, but one record shows a displacement of 8 mm. for such a change.

Discussion.

Dr. Chree thought the instrument ingenious and likely to be very useful for the purpose for which he understood it was primarily intended, viz., the observation of the disturbances produced at the National Physical Laboratory by existing and prospective electrical tramways and railways. There were various features in the existing disturbances whose investigation seemed likely to be of interest and to the public advantage. There were also certain natural phenomena, for example, "pulsations," or small oscillations of magnetic force, for whose investigation the instrument from its great sensitiveness seemed well adapted, only for such purposes it would have to be to be set up at some station, such as Eskdalemuir, remote from London or any other large centre of electrical industry. There were, however, two features, viz., the somewhat rapid variation of scale value across the sheet, and the fact that the instrument responded sensibly to changes of declination as well as horizontal force, which, he thought, stood somewhat in the way of its employment for ordinary *observatory* purposes.

Mr. R. S. Whipple asked whether the author had considered the advisability of flashing a spot of light across the sheet to give the time scale, as was done at Potsdam.

Mr. C. W. S. Crawley considered the tramways were a great nuisance to magnetic observers. He had gone a good deal further in sensitiveness than the author, and even when situated 16 miles from the nearest tramways he had found them very troublesome. The little kick in the middle of the disturbance which Mr. Smith thought might be an instrumental error had often been noticed by him, and was a definite phenomenon in no way due to the instrument.

Prof. T. Mather asked if the author had tried using the finest quartz fibre which he could handle. It appeared that the instrument took two or three seconds to attain its final position. If a finer fibre were used, a lighter and quicker magnetic system could be employed.

The Author, in reply, agreed with the remarks of Dr. Chree. He had thought it would be interesting to set up an instrument to detect very small pulsations, such as might occur during solar eclipses, while neglecting the larger ordinary disturbances. He admitted that the variation of sensitiveness across the sheet would be a disadvantage to an ordinary observatory assistant, but it gave him no trouble whatever. In reply to Mr. Whipple, he had already started to employ the flash of light method for the time

scale. In reply to Prof. Mather, there was no doubt that that the system could be made a good deal lighter if it were desired to measure very sudden disturbances lasting only a few seconds.

A paper entitled "*The Atomic Weight of Copper by Electrolysis*" was read by Mr. ALBERT G. SHRIMPTON.

Four copper-cells separating two silver cells were run in series. The areas of the four copper cathodes increased from 10 to 50 s.cs. By plotting the weights of the copper deposits against the corresponding areas of the cathodes, and extrapolating to zero area, the weight of the deposit is corrected for under experimental conditions. The atomic

$$\text{weight of copper} = \frac{\text{corrected weight of Cu}}{\text{mean weight of Ag}} \times 107.88 \times 2.$$

The mean atomic weight for ten determinations = 65·563, with a mean error of ± 0.003. To obtain a uniform coherent deposit of pure metal the following points were considered:—

1. Cylindrical cells with stationary and rotating cathodes were used.

The cathode current density must be kept below a certain *limiting* value to prevent the formation of non-coherent deposits, due to secondary deposition. This was found to depend upon the geometry of the cell, the concentration of the electrolyte, the presence of acids and other impurities, the addition of a porous pot, and the rate of revolution of the cathode. Formulæ are given by which the *limiting cathode current density* can be found for all conditions of the cell for Cu, Ag, Au, and Zn.

3. To prevent the formation of loose crystalline clusters the current density must also be kept below a certain value depending upon the weight to be deposited. (Formulæ are given).

DISCUSSION.

Mr. F. E. SMITH congratulated the author on the results of his work. He appeared to have triumphed over many difficulties, and for his particular purpose had converted the copper voltameter from an instrument of error into an instrument of precision. In future work he hoped that Mr. Shrimpton would avoid the use of common porous pots. They might produce trouble, and were not necessary, as all voltameter work could now be carried out without the introduction of any medium between anode and cathode. He should be pleased to give Mr. Shrimpton full particulars. The statement respecting deposition of hydrogen was, he thought, incorrect. It was not logical to assume that hydrogen ions were first deposited because of the lack of copper in the neighbourhood of the cathode, and then to state that as soon as they were deposited they went into solution again, and in doing so displaced copper from the solution. With regard to crystalline growths at the bottom of the cathode, he believed these were due to the high current density at the base due to the passage of the current through the liquid descending from the anode. There was also a possibility that the electrolyte was not quite pure. In the silver voltameter he had obtained striated deposits with impure electrolytes, but not with pure solutions. Mr. Shrimpton also stated that silver deposits from acidified solutions were normal; this was not his experience, nor that of other investigators. He believed the deposit to be less in mass when the electrolyte was acid. A rather important question arose with regard to any Cu_2SO_4 which might be formed in the cathode space. Richards (who also extrapolated to zero area, as Mr. Shrimpton had done) remarked in his paper: "A value obtained in this way must correspond to a deposit of copper slightly too great; for the mode of correction (*i.e.*, extrapolation to zero area) does not take account of the growing, although slight, presence of cuprous salts." Mr. Shrimpton said the extrapolation to zero area covered this case. The speaker thought the point was one that should be settled. Of course, when one reduced the area the current density at the cathode was increased, and so also was the fall of potential near the cathode; this might have some influence.

Dr. J. H. VINCENT mentioned that after working out the conditions necessary for satisfactory results, the author had performed the ten determinations quoted in the paper straight away, no results being rejected. As they all came within 1 part in 6000 of the mean there appeared to be no doubt that the correct conditions for satisfactory working had been obtained.

Dr. S. W. J. SMITH thought the author's views on secondary deposition could not be correct as they stood, although it was conceivable that sudden variations in the surface concentration of the copper sulphate, due to irregularities of convection, might make it possible for hydrogen to be deposited at one moment and to go into solution again at the next. Non-coherent deposits could be explained without invoking the aid of hydrogen. He thought the author's empirical conclusion, that the limiting current density depends upon the concentration of non-ionised molecules, had some theoretical support.

A paper entitled "*Note on an Improvement in the Einthoven String Galvanometer,*" by Mr. W. H. APTHORPE, was taken as read.

The instrument was exhibited at Cambridge on June 20.

NOTICES OF BOOKS.

A Manual of Practical Physical Chemistry. By FRANCIS W. GRAY, M.A., D.Sc. London: Macmillan and Co., Ltd. 1914.

THIS book contains a collection of exercises in physical chemistry, each of which can be performed by the student in a period of from two to three hours. Usually speaking the apparatus would have to be put together beforehand, and a few extra experiments are added which would require considerably more time for performance. Thermochemistry, polarimetry, and electrochemistry are included, and very clear diagrams of apparatus are given, while the directions are usually full and precise. In some cases help from a demonstrator might be required, but generally speaking the well-prepared student should be able to carry out the experiments quite unaided and calculate the results. The theoretical principles of the methods are shortly explained, and a very useful introduction on accuracy deals carefully with the calculation of average errors and similar questions.

Notes on Elementary Inorganic Chemistry. By F. H. JEFFERY, M.A. Cambridge: The University Press. 1914.

A CURSORY examination of this book suggests that it consists of a collection of disjointed facts and that it exhibits but little cohesion. But if the text is read more carefully it will be found that the author has very skilfully selected for notice the details which the beginner finds most puzzling or most difficult to retain in his memory. Occasionally it would appear that unnecessary matter has been included, such as the lists of salts, oxides, &c., but on the other hand some of the chapters, as for example those on oxidation and reduction, the identification of some common gases, and the action of heat upon salts and of acids on metals, are well planned. For revision purposes the book will be very useful, and although the ideal plan would be for the student to prepare such a summary for himself, basing it upon his lecture and laboratory work, if this is out of the question for lack of time the use of the book will certainly help to fix and establish his knowledge.

The Curious Lore of Precious Stones. By GEORGE FREDERICK KUNZ, A.M., Ph.D., D.Sc. Philadelphia and London: J. B. Lippincott Company. 1913.

THE author of this book has a unique knowledge of the uses of precious stones in religion, medicine, &c., and has moreover acquired what is believed to be the most com-

prehensive private library on the subject in existence. Hence he is particularly well qualified to produce a book which treats exhaustively of the use of precious stones at different periods by the peoples of all nations, and describes the many superstitions connected with them. The book is beautifully illustrated by coloured plates and double tones, and is full of curious anecdotes from old documents. The chapters on ominous and luminous stones and on crystals and crystal gazing are particularly interesting.

How to Build up Furnace Efficiency. By JOS. W. HAYS. Seventh Edition. Chicago: Jos. W. Hays. 1914.

THIS pamphlet contains a spirited discussion in highly colloquial language of the question of fuel economy and furnace efficiency, and is sure to make a considerable impression upon the practical man into whose hands it happens to fall. The author has had much experience in detecting defects in furnaces, and he has certainly profited by it. He has no false pride about confessing his mistakes, and he does not hesitate to take his readers into his confidence about "occasions on which he has made a fool of himself," and even provides an illustration to drive the lesson home. The book is written for the unlettered man who would be quite unequal to the task of tackling a treatise on fuel economy, and many anecdotes are given to illustrate the author's conclusions and to awaken the reader's interest.

Electric Switches for Use in Gaseous Mines. By H. H. CLARK and R. W. CROCKER. Washington: Government Printing Office. 1913.

THIS bulletin describes an interesting series of tests carried out with switches of both the explosion proof and oil types. The experiments were of a preliminary nature only, and were performed principally for the purpose of obtaining information upon which future tests could be based. Eight different types of switch are described in the bulletin, with criticisms of their designs and discussions of the results of the tests. Of the eight types only one was found to be really suitable for use in mines. The Bureau intends to carry out a further series of tests and to base upon them a list of switches suitable for use in gaseous mines.

Critical Ranges A2 and A3 of Pure Iron. By G. K. BURGESS and J. J. CROWE. Washington: Government Printing Office. 1914.

THIS bulletin contains a critical and historical summary of previous experimental observations of the location of the A2 and A3 points of pure iron, and also gives an account of a series of fresh experiments carried out by the authors. The thermal methods used were the inverse-rate method of Osmond and the derived differential method of Rosenhain, and special precautions were taken to ensure the accuracy of the results. The temperature ranged from 500—1000°, and the authors believe that they have established a definite transformation at 768°, and a less well-defined though more intense one at 898 to 909°.

The New International Metric Diamond Carat of 200 Milligrams. By GEORGE FREDERICK KUNZ.

THIS pamphlet contains a paper read before the American Institute of Mining Engineers at the New York meeting in 1913. It gives an account of the events which have led to the adoption of the metric carat, which is now legalised in most of the countries of Europe. There is no doubt that its adoption will be universal in the near future, and the advantages of using a single standard of weight in all countries, and one which moreover is decimally divided, are obvious. The pamphlet gives rules, with worked out examples, for calculating the weights and prices of diamonds under the new and old standards.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clviii., No. 18, May 4, 1914.

Chloro-iridate and Chloro-iridite of Lithium.—Marcel Delépine.—The compositions of the chloro-iridate and chloro-iridite of lithium are the same as those of the corresponding salts of sodium. In a mixture of the chloro-salts of lithium and sodium the latter separate first, with very little lithium. If the crystallisation is continued mixed crystals are obtained which, from $IrCl_6Na_2Li$ to $IrCl_6NaLi_2$, have a very much elongated crystalline form differing from the rhombohedric form in which the single sodium or lithium salts crystallise.

Bulletin de la Société Chimique de France. Vol. xv.-xvi., No. 10, 1914.

Preparation of Glycide.—Jean Nivière.—Bigot prepared glycide by the action of sodium on monochlorhydrine, but the process was very slow. The author has improved the yield and hastened the process by the following modification:—340 grms. of monochlorhydrine are mixed with three times their volume of absolute ether. The mixture is placed in a flask furnished with an ascending condenser and immersed in a water-bath. 65 grms. of sodium are gradually added in small portions of about 2 grms. The temperature is not allowed to exceed 40°. When all the sodium has disappeared the ethereal solution is decanted off, and the sodium chloride is washed with absolute ether and then with a mixture of ether and anhydrous alcohol. The ethereal solutions are distilled, and when the solvent is eliminated the residue in the flask is rectified *in vacuo*. Between 60° and 100° under 15 mm. glycide passes over.

Meconine Carboxyllic Acid.—P. Freundler.—Meconine carboxyllic acid is easily obtained by condensing opianic acid with potassium cyanide. At first a brown solution is obtained, which contains the potassium salt of the free oxy acid:—

$$(CH_3O)_2C_6H_2{<}^{CO_2H}_{CHO} + CNK =$$
$$= (CH_3O)_2C_6H_2{<}^{CO_2K}_{CHOH.CN}$$

When hydrochloric acid is added a brown viscous oil is deposited. This is probably the raw lactonic nitrile, and on saponification on the water-bath meconine carboxyllic acid is formed.

Berichte der Deutschen Chemischen Gesellschaft. Vol. xlvii., No. 7, 1914.

Syntheses of New Glucosides.—Emil Fischer.—The author, in collaboration with Helferich, has recently shown that the silver salts of the purines react with aceto-bromo-glucose in anhydrous solvents, and a simple synthesis of purin glucosides can be based upon this reaction. The author has now further shown that many other sugar derivatives can be prepared similarly. Thus aceto-bromo-glucose and dry silver succinimide react in xylol solution at the temperature of the water-bath, giving a good yield of tetra-acetyl-succinimide-glucoside. The acetyl groups can be removed by treatment with methyl alcohol ammonia, but at the same time a product, $C_4H_7O_2.C_6H_{11}O_5$, which appears to be the glucoside of succinamide, is formed.

INDEX.

END OF VOLUME CIX.